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HELIUM: ITS HISTORY, PROPERTIES, AND COMMERCIAL DEVELOPMENT.*

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THE story of Helium is one of the romances of science. There is probably nothing, unless it be the story of radium, which can compete with it in human interest. It represents one of the very best examples of a discovery in pure science which ultimately has a great commercial application.

In 1868 there was an eclipse of the sun which was visible in India. A number of scientific men were in India at the time making observations of the eclipse, and a spectroscope was for the first time turned on the solar chromosphere, that portion of the atmosphere of the sun, about ten miles deep, which merges into the corona. A bright yellow line was observed which was at first thought to be the sodium line. Janssen,[1] however, showed that this line was not exactly the same as the D_1 and D_2 lines of sodium, although extremely close to these lines. He, therefore, suggested that the line have the designation D_3. Frankland and

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[1] Janssen: *Compt. rend.*, 1868, 67, 838.

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Lockyer [2] decided that this line was due to a new element in the sun which had not previously been discovered on the earth and they suggested the name "Helium," from the Greek word "Helios," meaning the sun.

For a great many years nothing more was done in connection with this element. In 1888, Dr. W. F. Hillebrand,[3] of the United States Geological Survey, examined the gases which were evolved from certain uraninites when boiled with dilute sulphuric acid. Hillebrand obtained an inert gas which showed all of the properties of nitrogen. When sparked with hydrogen, in presence of hydrochloric acid, it gave ammonium chloride, and when sparked with oxygen, it gave oxides of nitrogen. The spectrum also was that of nitrogen. On the other hand, it was noticed that there were some lines in this spectrum which did not belong to nitrogen, and, in addition, after continuous sparking for a considerable period, there was a residue which diminished in volume very slowly. It is a great pity that American science was not responsible for the discovery of terrestrial helium. On the other hand, those who have worked with the rare gases can fully appreciate the difficulties attendant on work of this kind before the necessary technic was even partially developed.

In 1894, Sir William Ramsay, in conjunction with Lord Rayleigh,[4] made his memorable discovery of argon in the atmosphere, which discovery was announced at the British Association Meeting in the same year. After this discovery, Ramsay looked for other sources of the element. He heard through Sir Henry Miers of the observation of Doctor Hillebrand, described above, and suspected that the inert gas found by Hillebrand might be argon. He obtained a sample of the mineral clevite from Doctor Hillebrand, placed it in a tube connected with a Töpler pump, heated the mineral with sulphuric acid, pumped off the evolved gas, sparked the latter with oxygen, removed the excess of oxygen, and finally ran the purfied gas into a spectrum tube. The spectrum was entirely different from that of argon, having as a chief characteristic a bright yellow line. Sir William once described to the writer, in his characteristic manner, his surprise at what he

[2] Frankland and Lockyer: *Proc. Roy. Soc.*, 1868, 17, p. 91.

[3] Hillebrand, W. F.: On the Occurrence of Nitrogen in Uraninite, *U. S. Geol. Survey Bull.* 78, 1891, pp. 43–79.

[4] *Proc. Roy. Soc.*, 58, pp. 65–81, 1895. *Chem. News*, 71, p. 151, 1895.

saw when he put his small spectroscope to his eye. He was expecting to see the argon spectrum, consisting of lines more or less evenly distributed across the whole field of the instrument, or at least the bands of nitrogen. Instead, he observed a very brilliant yellow line, with two or three fainter reds, as many greens, and as many violets. These were more or less masked by slight impurities in the gas. His surprise was so great that he thought at first there was something wrong with his spectroscope, and took out his handkerchief and mechanically wiped the prism. Others were called in who suggested various explanations for the bright yellow line, the most common being that it was the sodium line due to dirty electrodes or other causes. It was only when the spectrum of the sodium flame was compared with the yellow line from the spectrum tube that it became evident, and beyond question, that a new element—terrestrial helium—had been discovered.[5] The wave-length was measured by Sir William Crookes,[6] and proved to coincide with that of the D_3 solar line.

As would be natural under such circumstances, it was not long before the work had its critics, and the elemental character of the gas was attacked. Runge and Paschen[7] showed that if the gas was allowed to pass through a porous plug, and from thence into an evacuated spectrum tube, the light at first obtained was greenish, afterwards gradually becoming yellow. At the same time, the intensity of the D_3 line increased. From this they thought that two gases were probably present, and by means of diffusion they had made at least a partial separation. This claim received some support from the fact that the density of helium obtained from minerals was not always constant, and varied within moderate limits. If helium from this source was allowed to diffuse through porous earthenware, fractions of different densities could be obtained.

Travers[8] proved that the difference of color in the spectrum was due to the difference in pressure in the tube. At extremely low pressures, the light given out was greenish in color, but as the pressure increased, the color became yellow and even orange

[5] Ramsay, Wm.: Discovery of Helium in Clevite, *Jour. Chem. Soc.*, 67, 1107.
[6] Crookes, Wm.: *Proc. Roy. Soc.*, **58**, 69, 1895.
[7] Runge and Paschen: *Phil. Mag.*, 1895 (v.), **40**, 297.
[8] Travers: *Proc. Roy. Soc.*, 1897, **60**, 449.

yellow. In addition, Ramsay and Travers [9] showed that by fractional diffusion helium from minerals could be separated into fractions of different density, but that these differences were due to traces of argon, which gas also was obtained from the minerals, in small quantity, mixed with the helium.

The presence of helium in the atmosphere was first discovered by Kayser [10] in 1895, and was confirmed by Friedlander.[11] Later the gas was shown to be a constituent of the gases evolved from numerous mineral springs and was also found in volcanic gases, and ultimately in certain natural gases, particularly in the United States.

The discovery of argon, followed by the discovery of helium, was the forerunner of the series of brilliant researches by Ramsay and Travers, which gave to the world five new elements, commonly called rare gases of the atmosphere, namely, helium, neon, argon, krypton, and xenon.

OCCURRENCE.

Helium, as already stated, is found in the atmosphere. Ramsay's first determination of the proportion was one part in 245,000 by volume. Watson,[12] using rather better methods, found what is probably a more accurate figure, namely, one volume in 185,000.

Samples of air at an altitude of several miles have been collected and analyzed for rare gases, and the percentage of helium found has always been approximately the normal one. J. H. Jeans [13] has done some theorizing on the proportion of helium in the atmosphere at different altitudes. His theory is that the atmosphere consists of more or less concentric layers containing different proportions of constituents. The proportion of helium does not vary materially unless a considerable altitude is attained, such as fifty miles, at which point the air consists mainly of nitrogen and hydrogen, with three times as much helium as oxygen. At 100 miles the atmosphere is principally hydrogen and helium, and at 500 miles it consists entirely of hydrogen and helium.

[9] Ramsay and Travers: *Proc. Roy. Soc.*, 1897, **60**, 206.

[10] Kayser: *Chem. News*, 1895, **72**, 89.

[11] Friedlander: *Zeitsch physikal Chem.*, 1896, **19**, 657.

[12] Watson: *Trans. Chem. Soc.*, 1910, **97**, 810.

[13] Jeans, J. H.: "The Dynamical Theory of Gases," chap. 15. Cambridge, 1916.

On this theory, a calculation of the total mass of helium in the atmosphere gives eleven billion tons.

Others do not agree with this theory. Dr. Johnstone Stoney [14] claims that the helium cannot be retained permanently by a planet of the size of our earth as the gas must be continually thrown off into space. The presence of helium in the atmosphere in constant proportions, therefore, depends upon a steady source of supply to make up the loss. Stoney's conclusion is supported by both Ramsay and Moureu.

Helium is found in very minute quantities in sea and river water, and in a large number of the older rocks and minerals. It undoubtedly exists in some of the fixed stars as well as in the sun, and its presence has been spectroscopically determined in many nebulæ.

Helium is found in the gases evolved from a large number of mineral springs. Moureu and Lepape [15] have done a considerable amount of work on determining the presence of the rare gases in gases evolved from mineral springs in France. Some springs give off gases containing a very considerable proportion of helium, that at Mazières containing over 5 per cent. of the rare gas and two springs at Santenay more than 8 per cent.

Locality.	Spring.	Nitrogen.	Argon.	Helium.
Aix-les-Bains	Alun		1.153	.037
Badgastein, Austria	Gratenbüker	97.25	1.181	.169
Bagnères-de-Luchon	Bordeu No. 2	96.45	1.25	.15
Bagnères-de-Luchon	Ferras	96.085	1.23	.285
Bagnères-de-Luchon	Saul No. 2	94.826	1.271	.323
Bourbon-Lancy	Lymbe	91.96	1.20	1.84
Bourbon-Lancy	Reine	96.1	1.15	1.75
Cauterets	César	98.55	1.275	.165
Cauterets	Raillère	98.508	1.377	.115
Grisy	Ys	95.5	1.18	2.18
Mazières	Romaine	91.46	.92	5.92
Nancy	Parc Sainte-Marie	95.36	1.29	1.60
Plombières	No. 3	94.505	1.375	.120
Plombières	No. 5	95.32	1.547	.104
St. Honoré	Crevasse	95.76	1.147	.893
Santenay (Cote d'Or)	Carnot			9.76
Santenay (Cote d'Or)	Fontaine Slaee			8.40
Uriaae		93.98	.938	.932

[14] *Chem. News*, 1895, **71**, 67.

[15] *Comp. rend.*, 1895, **121**, 819; 1904, **139**, 852; 1906, **142**, 1155; 1911, **153**, 740; 1911, **152**, 935. Moureu and Biquard: *Compt. rend.*, 1906, **143**, 795; 1908, **146**, 435.

In addition, the gases from the Bath Spring [16] in England are particularly rich in helium, and also carry as much as .24 parts of neon per 100 parts of nitrogen in the gas.

Very little work has been done along these lines in connection with springs in the United States. Recently, however, the Bureau of Mines has tested the gases evolved by a number of the geysers and hot springs in Yellowstone Park; for example, the Excelsior geyser, the Handkerchief pool, the pool near the north of Fountain Inn, a pool northeast of the Lion geyser, a pool near the Constant geyser in Norris basin, a muddy pool giving off sulphur dioxide close to the Monarch geyser, and a number of others. In no case was helium found in quantities sufficient to determine quantitatively in the sample taken. The actual volumes of helium evolved by some of the springs in France are quite large. Moureu and Lepape [17] have calculated some of these volumes and they have shown that the following volumes in cubic feet are evolved each year by the springs mentioned:

Santenay (Cote d'Or)	183
Neris (Allier)	1200
Bourbon-Lancy (Saone et Loire)	356
La Bourboule (Puy-de-Dôme)	108

Helium is found in certain volcanic and fumarole gases. The presence of the rare gas in Italian fumarole gases was determined as far back as 1898 by Nasini.[18]

The boracic acid fumaroles of Ladarello give off largely steam, the steam being used for generating power. The rest of the gas is carbon dioxide, with traces of hydrogen, methane, hydrogen sulphide, nitrogen, etc. The original analysis of Nasini showed something more than 90 per cent. carbon dioxide in the gas after the steam was condensed and from ten hundredths to fifteen hundredths of one per cent. helium.

Thorkelesson [19] examined gases from certain hot springs in Iceland. The analyses showed from .0006 to .0104 per cent. helium. The nitrogen content was high in many of the gases,

[16] Ramsay, Wm.: Report on the Mineral Waters of Bath, *Chem. News*, Vol. 105, 1912.

[17] *Compt. rend*, 155, 1912.

[18] Nasini, Anderlini, and Salvadori: *Gazz. chim. ital.*, Vol. 28, 1898, pp. 81–153. *Idem.*, Vol. 36, pt. 1, 1906, p. 429.

[19] Thorkelsson: *Danemark Mem.*, 7th Ser., Vol. 8, 1910, pp. 181–264.

some containing as much as 95 per cent. nitrogen. The percentage of argon was much higher than that of helium, namely from .01 to 1.93 per cent.

R. J. Strutt first systematically took up the investigation of the helium content of rocks and minerals. The helium cannot be determined directly in an igneous rock on account of the minute quantity present, but if it is assumed, as is probably the case, that the helium present is due to radioactive changes, if the radium present in the rock is determined, at least some very rough estimate of the probable helium content may be obtained. In the case of minerals containing thorium and uranium, the matter is very different, as the helium present can be actually measured quantitatively. This can be done in the following manner: If the mineral is soluble in sulphuric acid, a weighed quantity is placed in a heavy glass tube connected with a Töpler pump, and an arrangement made so that a sufficient amount of sulphuric acid can be introduced into the tube when desired without introducing air. The whole apparatus is exhausted and the acid brought in contact with the mineral. After complete solution and heating, the evolved gases are pumped off into a test tube over mercury. This gas is then sparked for several hours with some pure oxygen in presence of a small amount of strong caustic soda solution. This gets rid of all traces of nitrogen, the oxides formed being dissolved by the caustic soda. The partially purified gas is then run into another test tube over mercury and the oxygen removed by a globule of melted phosphorus. The phosphorus not only removes the oxygen, but the phosphorus pentoxide formed in the reaction dries the gas. This gas is then run into a burette and measured. Such a result gives the total amount of rare gas present which, in the case of minerals, is almost entirely helium. Some small traces of argon, however, are at times present. If desired, the argon can be removed by means of charcoal at the temperature of liquid air, and the helium pumped off can be remeasured.

If the mineral is not soluble in acid, the helium may be liberated by fusion with fusion mixture. Otherwise, the treatment is the same. A certain proportion of the helium in a mineral can also be obtained by heating the mineral direct without any chemical treatment. On heating monazite to 500° C. only a very small percentage of the helium is evolved. At 900° C., 24 hours heating is required to liberate all of the gas. For thorianite, 7 per

cent. is obtained at 300° C. after 5 hours heating, 8.5 per cent. at 500° C. after 80 hours, and the whole at 1000° C. after 30 hours. Usually helium is only found in measurable quantity in those minerals which contain thorium or uranium, such as carnotite, thorianite, pitch blende, etc.[20]

One mineral, beryl, has been found to contain a considerable amount of helium, and practically no radioactive matter from which the helium is supposed to be derived. Boltwood explains this on the basis that in the crystallization of the mineral only one of the shorter lived products of disintegration, such as radium or ionium, has remained with the mineral. This has decayed with the formation of helium, and as there was no uranium or thorium present, the mineral became inactive. This explanation, however, assumes no other possible origin for the helium than radioactive matter. Piutti[21] has found similar occurrences.

The volume of helium contained in any mineral depends upon several factors such as its geological age, the percentage of thorium or uranium present, and the density of the mineral which will largely control the leakage of the helium from the crystals.

The following table gives approximate volumes of helium which can be obtained from different minerals.

Mineral.	Observer.	Helium in c.c. for 1 gram of Mineral.
Clevite	Ramsay	7.2
Fergusonite	Ramsay	1.1
Fergusonite	Travers	1.813
Samarskite	Ramsay and Travers	1.5
Monazite	Strutt	2.41
Pitchblende	Ramsay and Travers	.30
	Strutt	.107
Thorianite	Buchner	8.2
	Strutt	8.9

[20] Ramsay: *Proc. Roy. Soc.*, 1896, **59**, 325. Ramsay and Travers: *Ibid.*, **60**, 442. Ramsay, Collie, and Travers: *Trans. Chem. Soc.*, 1895, **67**, 689. Olzewski: *Bull. Acad. Sci. Cracow*, 1905, p. 407. Bordas: *Compt. rend.*, 1908, 146, 896. Waters: *Phil. Mag.*, 1909 (vi.), **18**, 677; **19**, 903. Thomsen: *Zeitsch. physikal Chem.*, 1898, **25**, 112. Benedicks: *Bull. Geol. Inst. Univ. Upsala*, 1899, **4**, 1. Lange: *Zeitsch. Naturwiss.*, 1910, **82**, 1. Tschernik: *J. Russ. Chem. Soc.*, 1897, **29**, 291. Kitchin and Winterson: *Trans. Chem. Soc.*, 1906, **89**, 1570. Strutt: *Proc. Roy. Soc.*, 1908, A, **81**, 278. Hogley: *Phil. Mag.*, 1909 (vi.), **18**, 672. Piutti: *Le Radium*, 1910, **7**, 146. Strutt: *Proc. Roy. Soc.* (a), **76**, 1908, 80; *Ibid.* (A), **80**, 1908, 56. *Chem. News*, 1909, 99, 145, and many others.

[21] Piutti: *Le Radium*, **7**, 1910, 178. *Chem. Abs.*, **4**, 1910, 3055.

Strutt [22] has examined the saline minerals of Stassfurt and found not only that they contain helium in appreciable quantities, but also that the percentage of helium was very many times larger than could be justified by the uranium content of the mineral. The following table gives in a concrete form some of the results obtained:

Mineral.	Composition.	Helium, c.mm. per 100 grammes.	Grammes uranium oxide (U_3O_8) per 100 grammes.	Helium, c.c. per gramme U_3O_8.
Rock Salt.....	NaCl	0.0233	7.1×10^{-6}	3.3
Sylvine.....	KCl	0.55	2.15×10^{-6}	256
Carnallite.....	$KMgCl_36H_2O$	0.151	3.23×10^{-6}	47
Kieserite.....	$MgSO_4H_2O$	0.0179	6.47×10^{-5}	0.277

The following were also examined: kainite, krugite, astrakanite, längbeinite, polyhalite, schoenite, and tachydrite, and in none of these was the quantity of helium at all comparable with what was observed in carnallite or sylvine, but the D_3 line could nearly always be seen. Strutt stated that it was altogether improbable that the minute quantities of uranium and radium present could account for the helium content in the carnallite and sylvine. On the other hand, the helium in the rock salt was much of the order that could be expected from its geological age if the helium originated from the radioactive material present.

In 1907 Cady and McFarland [23] published a report on the presence of helium in a number of natural gases, mainly from Kansas. Some of the samples tested ran as high as 1½ per cent. helium by volume. The list on page 154 represents a selected number from results obtained by these authors.

It was pointed out that there seemed to be a distinct connection between the nitrogen and helium present, as in many cases the helium was in rough proportion to the nitrogen. It was the results of Cady and McFarland, on the natural gases of Kansas, that formed the foundation for the belief that an adequate supply of helium could be obtained from natural gas in the United States for use in balloons and dirigibles.

C. W. Seibel [24] has shown that not only is helium present in

[22] Strutt: *Roy. Soc. Proc.*, A, Vol. 80, 1908, p. 572. *Ibid.*, A, Vol, 81, 1908, p. 278.

[23] *Jour. Amer. Chem. Soc.*, 1907, **29**, 1524.

[24] *Met. and Chem. Eng.*, May, 1917.

Composition of Natural Gases.

No. Locality.	Oxygen O_2	Carbon Dioxide CO_2	Olefines C_nH_n	Carbon Monoxide CO	Methane CH_4	Ethane C_2H_6	Hydrogen H_2	Helium He	Nitrogen N_2
1 Dexter, Kansas	0.20	.00	.....	.00	14.85	.41	trace	1.84	82.70
6 Dexter (Greenwell well), Kansas	.10	.00	.00	.00	14.33	1.06	trace	1.64	82.87
41 Eureka new well, Kansas	.10	.20	.00	.00	51.80	.00	.00	1.50	46.40
9 Fredonia, Kansas	trace	.61	.12	.00	82.25	.00	.00	.616	16.40
4 Eudora, Kansas	.31	.62	.00	.00	88.60	.00	.00	.27	10.20
37 Augusta, Kansas	.00	.00	.77	.00	79.10	7.44	.00	.25	12.44
20 Moran, Kansas	.20	.30	.35	.20	92.00	.00	.39	.214	6.35
24 Butler, Ohio	.05	.00	.40	.00	70.00	16.75	.27	.15	12.38

these natural gases, but also small quantities of the other rare elements, even krypton and xenon.

Moureu and Lepape [25] and Voller and Walter [26] have pointed out that very small quantities of helium are contained in certain natural gases in Europe, but the quantities are extremely small and the occurrences unimportant.

PROPERTIES.

Up to the present, no one has succeeded in combining helium with any other element or getting the gas to take part in a chemical reaction under any conditions whatever. In this respect it is similar to argon and the other rare gases. Shortly after helium was discovered Ramsay and Collie [27] carried out an exhaustive series of experiments in order to test the chemical inertness of the gas. A definite volume of helium was passed over a series of substances heated to a bright red heat. The helium was finally pumped off and measured, and the substance used was reheated, and any evolved gas was collected and measured. In no case was there any change in the volume of the helium, and in every instance the other substance was apparently unaffected. Sodium, phosphorus, zinc, cadmium, and arsenic were all distilled in the gas, and the following substances were also strongly heated: glucinum, silicon, boron, magnesium, thallium, titanium oxide and

[25] *Compt. rend.*, **155**, pp. 197–200, 1912.
[26] *Hamburger Wiss. Inst.*, **28**, 1910.
[27] *Proc. Roy. Soc.*, 1896, **60**, 53.

magnesium, thorium oxide and magnesium, sulphur, selenium, antimony, bismuth, metallic cobalt, platinum black, soda lime and potassium nitrate, and soda lime and sulphur. The gas has also been sparked, and strongly heated with all other known gases without result.

Sieverts and Bergner [28] have shown that helium is not soluble in certain solid or liquid metals, such as gold, nickel, silver, copper, iron, palladium, uranium, aluminium, magnesium, etc.

If fergusonite is heated to 600° C. it suddenly begins to glow, and the gas which is evolved consists very largely of helium, namely between 70 and 80 per cent. The heat evolved is considerable, being more than 800 cal. per gram of mineral. This might indicate that helium was held in the mineral in combination. On the other hand, it has been pointed out by Travers [29] that a similar phenomenon sometimes occurs with minerals which do not contain helium. An examination of the rate of production of helium from minerals, both by means of heating, and by fine grinding *in vacuo*, seems to indicate that the helium is contained in the mineral in very minute cavities, and not in actual combination.

It has been suggested that the splashing of the electrode metal observed on the side of a Geissler tube containing helium and the other rare gases is due to an endothermic compound. There is, however, no definite proof of such an assertion.

Solubility.—Antropoff [30] has determined the solubility of helium in water. He obtained the following results for the absorption coefficient: 0° C.–.0134, 10° C.–.0100, 20° C.–.0139, 30° C.–.0161, 40° C.–.0191, 50° C.–.0226. More recent results,[31] obtained by Antropoff, gave the following corrected values: 0° C.–.00967, 10° C.–.00991, 20° C.–.00996, 30° C.–.01007, 40° C.–.01029, 50° C.–.0108. The existence of a minimum is not unusual, as it is found in the case of other inert gases, and also hydrogen.

Thermal Conductivity.—The thermal conductivity of helium has been studied by Schwarze.[32] If, in the equation $K = f.n.c_v$, n and c_v are the viscosity and the specific heat at constant volume

[28] *Ber.*, 1912, **45**, 2576.
[29] *Nature*, 1905, **71**, 248.
[30] *Proc. Roy. Soc.*, 1910, A, **83**, 474.
[31] *Zeitsch. Elektrochem.*, 1919, **25**, 269–297.
[32] *Physik. Zeit.*, **4**, p. 229; 1903. *Ann. Physik.* (4), 11, pp. 303–330, 1903.

respectively, and f is a constant, then K is the thermal conductivity of the gas for helium. At 0° C., K was found by Schwarze to be .0003386.

Viscosity.—Schultze [33] found that the viscosity of helium at 15° is 1.086 times the viscosity of air. Rankine [34] later repeated the work using different apparatus, and confirmed Schultze's figure.

If the absolute value for the viscosity of air is taken at 15.5° C., and is $n = 1.803 \times 10^{-4}$ *C.G.S.* units, then the viscosity of helium at 15° is 1.958×10^{-4} *C.G.S.* units.

Density.—The density of helium has been determined by a number of observers. The following results have been obtained (oxygen = 16): 1.979,[35] 2.00,[36] 1.99,[37] 1.995,[38] 1.999.[39] It is probable that the determination of Watson of 1.995 is as accurate, if not more so, than any of the others.

The atomic weight and molecular weight of helium are, of course, the same since the gas is monatomic, and the figure 4 is generally accepted. A recent determination by T. S. Taylor [40] gives the weight of a normal liter of helium (oxygen = 16) as 0.17850 ± 0.000015. The molecular weight (oxygen = 32) is 4.0008 ± 0.0005.

Dielectric Cohesion.—Helium conducts a current better than any known gas except neon. The dielectric cohesion of helium is 18.3, air being 419, argon 38, and neon 5.6.[41] This property of helium is readily illustrated by means of a tube containing movable electrodes in which certain gases can be introduced, and held at definite pressures. With the same difference of potential, pressure, etc., oxygen gave a spark of 23 mm.; hydrogen, 39 mm.; argon, 45.5 mm.; and helium 250 mm.[42]

Refractivity.—This property of helium was first determined

[33] *Ann. Physik.*, 1901 (iv), **6**, 302.
[34] *Proc. Roy. Soc.*, 1910, A, **83**, 265.
[35] Ramsay and Travers: *Proc. Roy. Soc.*, 1898, **62**, 316.
[36] Olszewski: *Ann. Physik*, 1905 (iv), **17**, 997.
[37] Onnes: *Comm. Phys. Lab. Leyden*, 1908, No. **108**.
[38] Watson: *Trans. Chem. Soc.*, 1910, **97**, 810.
[39] Heuse: *Ber. deut. physikal Ges.*, 1913, **15**, 518.
[40] *Phys. Rev.*, **10**, 653–60 (1917).
[41] Bouty: *Compt. rend.*, 1907, **145**, 225. *Ann. Chim. Phys.*, 1911 (viii), **23**, 5; 1913 (viii), **28**, 545.
[42] Collie and Ramsay: *Proc. Roy. Soc.*, 1895, **59**, 257.

by Rayleigh, but his figures were not correct. Ramsay and Travers [43] repeated the measurements and determined the refractivity of helium ($\mu - 1$) to be 0.1238 times that of air which gives the value of μ as 1.0000361. Other observers [44] have obtained slightly lower figures than Ramsay and Travers.

Ratio of Specific Heats.—The ratio of specific heats at constant volume has been determined by a number of observers theoretically. This ratio for a monatomic gas should be 1.667. Ramsay found 1.652, and Scheel and Heuse [45] found 1.660 at 18° and 1.673 at −180°.

Specific Heat.—Cp equals 1.2662 ± 0.0011. This figure was determined by Ramsay and Rudorf [46] after carefully taking the weighted averages of the different determinations on the specific heat of the gas. The molecular heat MCp at 18°, according to Scheel and Heuse, is 4.993, and at −180° is 4.934.

Isotopes.—According to J. J. Thomson and F. W. Aston,[47] helium has no isotopes, as shown by the positive ray method of Thomson. This is in contradistinction to neon, which has two isotopes of mass 20 and 22, respectively, and a third doubtful one of mass 31. According to these authors, argon has two isotopes, krypton six, and xenon five.

Spectrum.—Travers [48] found that the color of the discharge through a vacuum tube containing helium depended upon the pressure of the gas, and that the following colors were observed as the pressure got less and less: orange, yellow, bright yellow, greenish yellow, and green. Runge and Paschen [49] found that the spectrum of helium contained six series of lines which fall into two groups, each group consisting of a special series and two secondary series. The first group consists of doublet series and the doublet D_3 is the principal line of this group. It is the lines of this group that are commonly seen in a spectrum tube when the tube is emitting yellow light and the lines of this group are also the ones seen in the chromosphere of the sum. The chief line of

[43] *Proc. Roy. Soc.*, 1901, **67**, 331.

[44] Scheel and Schmidt: *Ber. deut. physikal. Ges.*, 1908, **6**, 207. Burton: *Proc. Roy. Soc.*, 1908, A, **80**, 390.

[45] Sitzungsber, K.: *Akad. Wiss.*, Berlin, 1913, p. 44.

[46] Ramsay and Rudorf: "Oswald-Drueker," Vol. 11, p. 121.

[47] *Phil. Mag.*, **39**, 611–25, 1920.

[48] *Proc. Roy. Soc.*, 1897, **60**, 449.

[49] *Phil. Mag.*, 1895 (v), **40**, 297.

the second group has the wave-length 5015.73 in the green, and the lines of this group become more prominent at a lower vacuum when the light emitted from the tube is greenish or yellowish green. The wave-lengths of the D_3 doublet are given by Runge and Paschen as 5876.21 and 5875.88. The measurements of some of the principal lines by different authors are given below:

Runge and Paschen.	Rayleigh I.	Rayleigh II.	Eversheim.
7065.48	7065.192	7065.200	7065.207
6678.37	6678.147	6678.150	6678.151
5875.870	5875.618	5875.625	5875.639
5015.732	5015.682	5015.680	5015.683
4922.096	4921.927	4921.930	4921.934
4713.252	4713.079	4713.144	4713.154
4471.646	4471.480	4471.482	4471.493

Lyman [50] calls attention to a new helium series in the extreme ultra-violet. With a powerful disruptive discharge, a sharp, fairly strong line appears at 1640.2. No trace of this line is found in hydrogen under the same electrical condition, and it does not occur in helium when the discharge circuit is free from capacity. Under the same violently disruptive condition, the line at 1216, always present in helium and hydrogen, develops a satellite on its more refrangible side, of apparent wave-length 1215.1.

Liquefaction of Helium.—Hydrogen on expansion through a nozzle becomes warmer instead of cooler. If hydrogen, however, is cooled by liquid nitrogen boiling under reduced pressure the value of K with the Joule-Thomson effect changes sign, and hydrogen, therefore, can be cooled and liquefied by nozzle expansion. The same condition exists for helium. This gas has to be cooled by liquid hydrogen boiling under reduced pressure to a temperature of 15° C. absolute before expansion in order to produce liquefaction.

Helium was first liquefied by Professor Onnes [51] of the University of Leiden, in 1908, using the method described above. About 60 cubic centimetres of liquid were finally obtained and with this the physical constants of the gas were determined.

A very considerable quantity of the gas which Onnes used was supplied to him by Dr. H. S. Miner, of the Welsbach Com-

[50] *Science*, November 21, 1919.

[51] *Proc. K. Akad. Wetensch*, Amsterdam, 1908, 11, 168. *Compt. rend.*, 1908, **147**, 421.

pany, who has always been generous in assistance of this character to scientific research. A few months ago Professor Onnes was supplied by the U. S. Government with 800 cubic feet of helium obtained at the Texas plants. This material will give Onnes ample opportunity to extend his researches in connection with liquid helium.

Liquid helium is mobile and colorless. Its density determined at different temperatures is as follows:

D.	T. abs.
.1208	4.33
.1216	4.29
.1275	3.98
.1393	3.26
.1459	2.40[82]

Next to liquid hydrogen, it is the lightest liquid known. Its maximum density is at 2.2° absolute. The calculated refractive index is 1.03. The surface tension is small, and the boiling point is 4.25° absolute. The critical temperature is 5.25° absolute, and the critical pressure 2.26 atmospheres. Solid helium has not yet been obtained.

RELATION OF HELIUM TO RADIOACTIVE CHANGES.

Radium, when associated with its disintegration products, gives off three types of rays: alpha, beta, and gamma. The first travels twenty thousand miles a second, and has low penetrating power, being stopped by a thin sheet of paper. The beta rays are small in mass, namely about 1/1600 that of a hydrogen atom, but have high velocity, and moderately high penetrating power. Beta rays will pass through an ordinary thin piece of glass tubing and have a velocity of from one hundred thousand miles per second up to that of light. The alpha rays are positively charged, and the beta rays negatively charged. The gamma rays are vibrations in the ether similar in character to X-rays, but of much shorter wave-length, and have a higher penetrating power than X-rays.

After it was shown that the mass of the alpha particle was comparable to that of the helium atom, Rutherford stated that the alpha particle undoubtedly was a helium atom carrying two posi-

[82] Onnes: *Comm. Phys. Lab.*, Leyden, No. 119.

tive charges. It remained for Ramsay and Soddy[53] to prove this statement by actual experimentation. They dissolved a radium salt in a little water in a tube which had been previously evacuated, and collected the gases which were evolved. These were purified and were shown to contain helium. On allowing the radium solution to stand, and pumping off the gases once more, a second amount of helium was obtained after proper purification. In other words, helium was being formed constantly from the radioactive changes going on in the solution.

When a radioactive change takes place, therefore, with the elimination of the alpha particle, it means that since helium has an atomic weight 4, the atom which is produced by the change has an atomic weight which is equal to that of the first element minus 4. For example, in Table I, the radium emanation atom explodes with the elimination of an alpha particle, and gives a new atom Radium A with an atomic weight 218 which is less by 4 than the atomic weight of radium emanation mentioned, namely 222. It can be readily seen in the table that wherever an alpha particle is eliminated in the radioactive change this condition maintains. The table is not complete for the sake of simplicity, but it is sufficient to illustrate the point under discussion.

TABLE I.

The Uranium-lead Radioactive Series.

	Atomic weight.	Rays.	Half-life period.
Uranium 1	238	Alpha	5×10^9 years.
Uranium X_1	234	Beta	23.5 days.
Uranium X_2	234	Beta and gamma	1.11 min.
Uranium 2	234	Alpha	2×10^6 years.
Ionium	230	Alpha	10^5 years.
Radium	226	Alpha and slow beta	1,690 years.
Radium emanation	222	Alpha	3.85 days.
Radium A	218	Alpha	3.05 minutes.
Radium B	214	Beta and gamma	26.8 minutes.
Radium C	214	Alpha, beta and gamma	19.5 minutes.
Radium D	210	Beta and gamma	16.5 years.
Radium E	210	Beta and gamma	4.85 days.
Radium F (polonium)	210	Alpha	136 days.
Radium G (lead)	206	.....	.....

As already shown in the earlier part of this paper, radium is widely disseminated through the earth's crust in rocks and

[53] *Proc. Roy. Soc.*, V, 72, p. 204, 1903.

minerals. Although the amounts are locally extremely small, the total in the earth's crust is relatively large. It has been generally believed that helium in the atmosphere has been derived from radioactive changes in the earth's crust, and radioactive changes have also been generally accepted as the origin of the helium in gases from mineral springs, etc. Such an explanation does not account for the neon and other rare gases in the atmosphere nor for the neon which has been found in the gases of certain springs. The classic work of Ramsay and Cameron [54] has shown that if a solution of copper nitrate were treated with radium emanation not only was lithium found in the solution, but the gas which was afterwards pumped from the bulb, consisting mostly of hydrogen and oxygen from the decomposition of the water, after proper purification gave the argon spectrum, but showed no helium lines. The gas, however, contained .34 cubic centimetres of nitrogen. When distilled water was treated with the emanation, neon with a trace of helium was obtained, but no argon. There was present, however, .307 cubic centimetres of nitrogen. This work has not been generally accepted owing to the fact that the neon can be detected in extremely small quantities of air, and it has been assumed that there was probably some leak in the apparatus used.

Other work has at least indicated the possibility of results of this character. Collie and Patterson,[55] working separately, obtained identical results, which seem to indicate the possible formation of neon with traces of helium by the passage of an electrical discharge at low pressure in hydrogen.

Mason [56] obtained results of a similar character. Others, particularly Strutt, were not able to duplicate the results and the whole matter has been left in a rather unsatisfactory condition.

Radioactive changes take place at a very definite rate. The half-life period (see Table 1) represents the time required for half of any particular radioactive element to change into the next disintegration product. For example, the half-life period for radium emanation is 3.8 days, which means that starting with any definite quantity of the emanation, after 3.8 days we would have

[54] *Jour. Chem. Soc.*, **91**, 1593. *Ibid.*, **93**, 996. *Ibid.*, **93**, 992.

[55] *Trans. Chem. Soc.*, 1913, **103**, 419. *Proc. Chem. Soc.*, 1913, **29**, 217. *Proc. Roy. Soc.*, 1914, A, **91**, 30.

[56] *Proc. Chem. Soc.*, 1913, **29**, 233.

half of the original gas left. At the end of a second similar period, half of what was left would be changed, and we would, therefore, have actually one-quarter of the original amount. In other words, the element changes according to an exponential law. This being so, it is not difficult to calculate the volume of helium that can be obtained from any given weight of a radioactive element, and we find that the volumes so obtained are extremely small. Two thousand pounds of uranium metal, together with all its disintegration products in equilibrium will only produce 110 cubic millimetres of helium per year. It can, therefore, be readily seen that in order to give the total volume of helium which is in the atmosphere a very considerable time, even from the geological standpoint, must have elapsed for the necessary radioactive changes to have taken place. It also shows that in order to account for the helium evolved in gases from certain mineral springs there must have been a very large portion of radioactive material available within the area through which waters of the springs percolate.

COMMERCIAL PRODUCTION OF HELIUM.

Use of Dirigibles During the War.—Before the war the Germans had spent many years in the development of a type of dirigible which received the name of zeppelin, after Count Zeppelin, its inventor. These ships were constructed of a number of separate compartments, and had a rigid frame work built either of aluminum or later of an alloy of aluminum, called duralumin, which has a tensile strength of mild steel and a specific gravity only a little heavier than that of aluminum. With a capacity of from one to two and a half million cubic feet of hydrogen, these vessels were able to travel at from 50 to 75 miles per hour, and to make long journeys without serious trouble. A trip of one thousand miles was a small undertaking, and even two thousand miles was not impossible. Since the war the feat of the R34, a British dirigible, in crossing the Atlantic is typical of what may be expected from these monsters of the air.

In the early stages of the war, the Germans used their dirigibles largely for bombing purposes, particularly over London and the munitions districts of England. Although the damage done from these bombing excursions was somewhat minimized at the time, there is no question, from post-war information, that

the damage was much greater than the public was allowed to believe while the war was in progress.

Another use for the dirigible which did not appeal so strongly to the public, but which was recognized by military and naval men as probably being more important than the one already mentioned, is the special adaptability of the dirigible for scouting purposes. The Germans used their air fleet to good purpose along this line. The German fleet would never venture from port without two or three dirigibles floating overhead, and these were able to inform the fleet below at all times of the near approach of British war vessels. In this manner, the German fleet could or could not, as it saw fit, accept battle or retire to its base. It has been stated that at the battle of Jutland a dirigible circulating above the Grand Fleet kept the Germans fully informed of the position of the British battleship division while they were engaging the British armored cruisers.

Colonel F. Lucas, in charge of British dirigibles during the war, informed the writer that if it had not been for the German dirigibles he had no doubt but the British fleet would have caught and destroyed the German fleet. The British claimed that one dirigible was equivalent for scouting purposes to six fast cruisers.

The French and British had no dirigibles at the start of the war, but later made haste as rapidly as possible to repair the deficiency. They recognized, however, on account of the experience they gained from the defence of London and other important points in England that the dirigible was not only vulnerable, but extremely so against a well-organized attack. The Germans recognized this also, and, therefore, invariably made their attacks on England at night, and operated from a high altitude in order to minimize attacks by airplane, for a single incendiary bullet fired into a dirigible would probably bring the huge ship down within a few moments a mass of flames. The inflammability of the hydrogen was the one weak spot in this method of attack, and the British realized this quite early in the war. In addition, the constant danger of such a death had a strong effect on the nerves of the operating crews, so that, perhaps, the dirigibles were not as efficient as they otherwise might have been.

The answer, of course, was a non-inflammable gas sufficiently light to take the place of hydrogen as a lifting force. There is only one gas known which has these qualities, namely, helium.

The use of helium would have still further advantages. It diffuses through a fabric at about 75 per cent. of the rate of hydrogen. Owing to the non-inflammability of the gas, it would be possible to put the engines up in the framework of the dirigible, and in this way get a direct drive giving very much increased speed for any given horse-power. On the other hand, it would be necessary to make some improvements in the design of the dirigible in order to prevent waste of gas by valving. The Army and Navy Air Services are working on these problems at the present time.

Initiation of the Helium Project.—As already stated, helium is found in the atmosphere to the extent of one part in 185,000 by volume. It is found in gases from springs, etc., but during the early stages of the war neither the French nor British seemed to have any knowledge of a source of helium that would be sufficient for the purpose outlined.

On February 28, 1915, Sir William Ramsay wrote a personal letter to the writer in which, among other things, he said, " I have investigated blowers, that is, coal-damp rushes of gas, for helium for our government to be used in dirigibles. There does not appear to be anything in the English blowers, but I am getting samples from Canada and the States." He then proceeded to state that personally he did not feel that the idea was at all practical, and also expressed his opinion that, owing to the fact that airplanes could operate successfully against dirigibles, their use was not as important as the Admiralty seemed to believe. At the time this letter was received, the writer was fully aware of the work of Cady and McFarland on natural gases of Kansas, already described, although Ramsay and the British scientific men apparently had forgotten this work. It was, therefore, a question of whether Ramsay and the British government should or should not be informed concerning this work of Cady and McFarland. At the time, all government officials were being strongly urged by frequent communications to remain neutral in every sense of the word, and after several weeks of deliberation, the writer decided not to inform Sir William of the large source of helium which was available in Kansas in the natural gas wells of that State. Whether he was or was not right in this matter is a question for individual judgment.

In April, 1917, the writer attended a meeting of the American

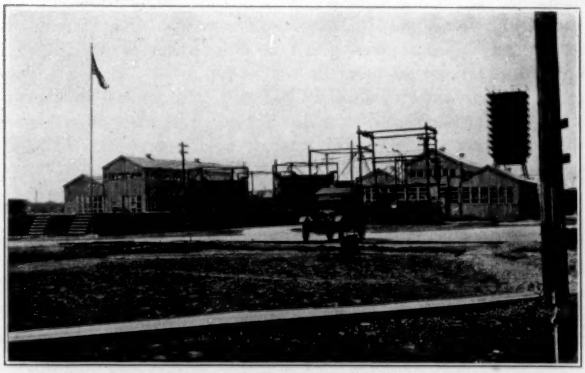
Chemical Society in Kansas City, Missouri, where a paper on the presence of rare gases in certain natural gases of Kansas was read by Mr. C. W. Seibel, of the University of Kansas, who had worked under Doctor Cady. Following this paper, in the open discussion, the writer mentioned the possible use of helium in dirigibles and advocated that the matter be taken up seriously. Mr. G. A. Burrell, of the Bureau of Mines, had, a short time before this, learned of the interest of the British in helium, and had also recognized the possibilities of the natural gases of Kansas as a source of supply. In the following June, the whole question was brought to the attention of Dr. F. G. Cottrell and Dr. Van. H. Manning, Director of the Bureau of Mines, and approval was given by the Director to Messrs. Burrell and Moore to take the matter up with the Army and Navy. Major (now Colonel) Chas. DeF. Chandler, in charge of the Balloon Division of the Air Service, was interviewed, and he immediately showed great interest in the project. Colonel Chandler deserves great credit for his broadmindedness and foresight in connection with this whole work. The matter was also brought to the attention of the Navy officials, and they became also intensely interested. Commanders A. K. Atkins and H. T. Dyer and Mr. G. O. Carter represented the Navy, and it is due to the interest of these men and Colonel Chandler that the necessary funds were ultimately made available, and the helium project was actually made possible. The importance of the production of helium as a war measure received considerable impetus about this time from a visit to this country of Commander C. D. C. Bridge and Lt. Commander L. C. Locock, of the British Navy, for which visit Major R. B. Owens, Secretary of the Franklin Institute, was largely responsible.

In order to separate helium from natural gas, it was necessary to use a refrigeration process which would liquefy everything present except the helium. To do this, since the helium-bearing natural gases were high in nitrogen, it was necessary to ultimately reach the temperature of liquid nitrogen, namely -195.7° C. The separation of oxygen from nitrogen by refrigeration methods had taken a very considerable period of experimentation and involved a large outlay of capital. This meant separating 21 per cent. of one gas from 79 per cent. of the other. If in the preparation of oxygen a purity of 98½ per cent. is obtained, the result is

considered satisfactory. In obtaining helium from natural gas, however, it would be necessary to start where the other work left off, owing to the fact that the gas to be treated would contain not more than one per cent. helium. The undertaking, therefore, was an extremely difficult one.

For this reason, it was decided to use three processes, hoping that one at least would solve the problem quickly and efficiently. At the time there were two commercial companies in this country making oxygen from liquid air, namely, the Air Reduction Com-

FIG. 1.



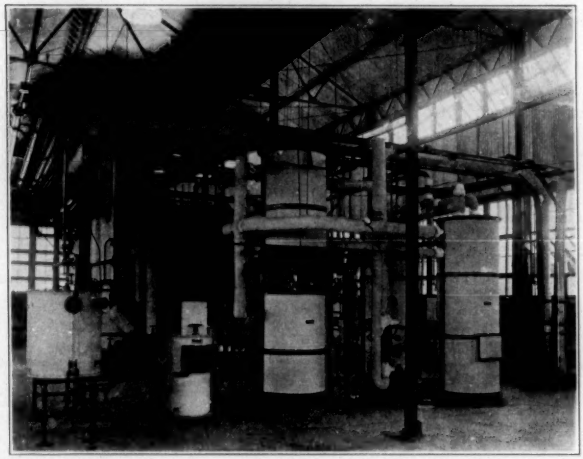
Exterior of Plant 1 (Linde System), Fort Worth. The building on the right is the compressor building, and on the left the "process" or refrigeration building.

pany of New York, using the Claude process, and the Linde Air Products Company of New York, using the Linde process. In addition, the Bureau of Mines through Dr. Cottrell had been in touch with Mr. F. E. Norton, who had a process which could be applied to this work called the Jefferies-Norton process.

Funds were allotted to the Bureau of Mines for the erection of three experimental plants, representing the three processes described above. Two of these plants (the Air Reduction and the Linde) were placed at Fort Worth, and the third (Jefferies-Norton) was located at Petrolia, Texas. The reason for this location was that the Bureau of Mines, making a quick survey, had found that the natural gas in the Petrolia, Texas,

field contained .93 per cent. helium. In addition, the volume of the gas was reasonably large, since it was possible at the time in question to pump as much as fifteen million cubic feet of gas per day from the wells. This gas was piped to Fort Worth, Dallas, and other towns, and an arrangement was made with the Lone Star Gas Company, of Fort Worth and Dallas, to use this gas from the main pipe line, and allow the return of the processed

FIG. 2.



Interior of Process Building, Plant 1, Fort Worth. Forecoolers and interchangers are shown in this picture. The column or still is hidden by the rest of the equipment.

gas after the helium had been extracted to the pipe lines of the company going to Fort Worth and Dallas. This meant that the government would only have to pay for the actual loss of gas during the processing.

Meanwhile, some small developments along similar lines had been going on in Canada. Professor J. C. McLennan, of Toronto University, had been asked by the British Admiralty to also look for sources of helium, and he had located two sources of natural gas in Canada carrying helium, namely, in Ontario and Alberta. The helium content was respectively .34 and .33 per cent., and it

has been estimated that the two sources together would give a possible supply of ten million cubic feet of helium per annum. In 1917, a small experimental station was set up at Hamilton, Ontario. Very little progress was made for a considerable time, and in 1918 it was only possible to raise the percentage of helium in the gas to 5 per cent. In the fall of 1918, another station was established at Calgary, Alberta, and more rapid progress was made from that time. The first product contained about 5 to 6 per cent. helium, and this was re-processed until the purity was from 85 to 90 per cent. The total volume of helium produced in a run rose from about 300 cubic feet to more than 700 cubic feet. The plant, however, was small, and the operations rather intermittent, and after the war the plant was shut down. Efforts to obtain sufficient capital to make enlargements and improvements since the war have not been successful.[57] Associated with Professor McLennan were Professor John Satterly and Mr. J. Patterson, who were responsible for a good deal of the success attained.

Whereas the Canadians actually began on their experimental work a little before we did in this country, there was no comparison between the rapidity of progress achieved. Plants No. 1 (Linde process) and No. 2 (Air Reduction) were able to get started considerably before Plant 3 (Jefferies-Norton), as the equipment they used was largely their standard equipment for making oxygen and nitrogen. Necessary modifications, however, were introduced later on. Plant No. 1 commenced to operate March 6, 1918, and made its first helium on April 8, 1918, when some gas analyzing 27 per cent. helium was obtained. This purity was increased after a few months, until in the early part of July a grade of over 70 per cent. was obtained, and in September the plant was operating very consistently, producing an average of from 4000 to 6000 cubic feet of 70 per cent. helium during each operating day. It was necessary to re-process the gas in order to raise its purity to what was desired, namely, over 90 per cent. The impurity of the 70 per cent. material consisted almost entirely of nitrogen, but if the grade of the gas dropped below 60 per cent. helium, there was a small amount of methane in the mixture as well as hydrogen. The methane, as well as the nitrogen, was easily removed by re-processing.

[57] McLennan: Helium, Its Production and Uses, *Jour. Chem. Soc.*, **693**, p. 923, 1920.

Plant No. 2 began to operate May 1, 1918, and very quickly obtained some helium, as, on May 13, they produced some gas of a grade between 60 and 70 per cent. helium. The operations of Plant 2, however, were as a whole not as successful as those of Plant 1. This was partly due to the fact that more energy and interest on the part of the parent company was put into Plant 1. Apparently the Linde Company had a conception of the importance

FIG. 3.

Inside view of Plant 2 (Air Reduction Company), Fort Worth. The still and interchangers are shown in the centre background; the tops of the calcium chloride driers just behind the motor and the carbon dioxide removers to the far right.

of the project and made every endeavor to make it a success. The engineering force in connection with Plant 2, however, was thoroughly efficient and alive to the value of the work, especially the chief engineer of the Air Reduction Company, Mr. M. H. Roberts. In addition, the policy adopted by the Linde Company of looking ahead, and having on the ground the necessary material for a change in plant operation provided what was being tried out was not a success, did more toward obtaining their ultimate success than did the actual superiority of their process over the Claude process used by the Air Reduction Company.

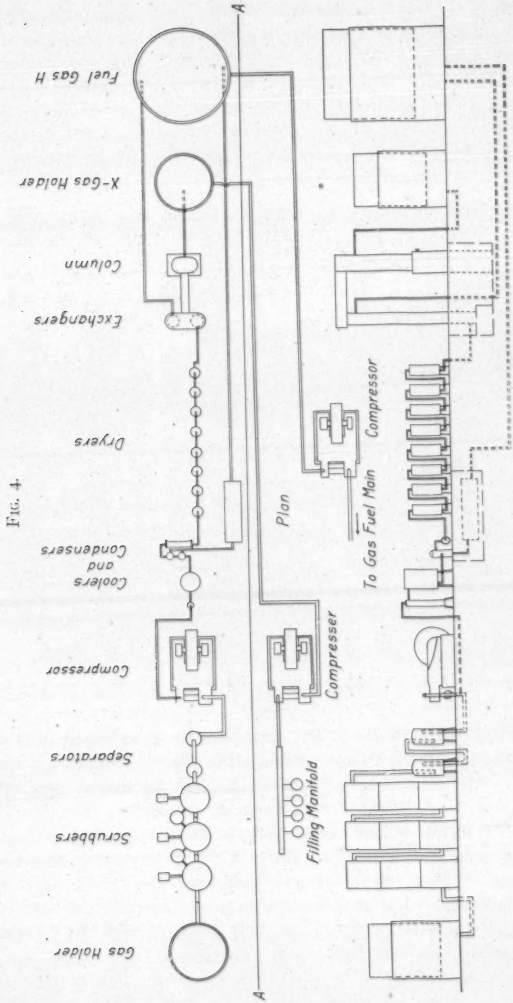
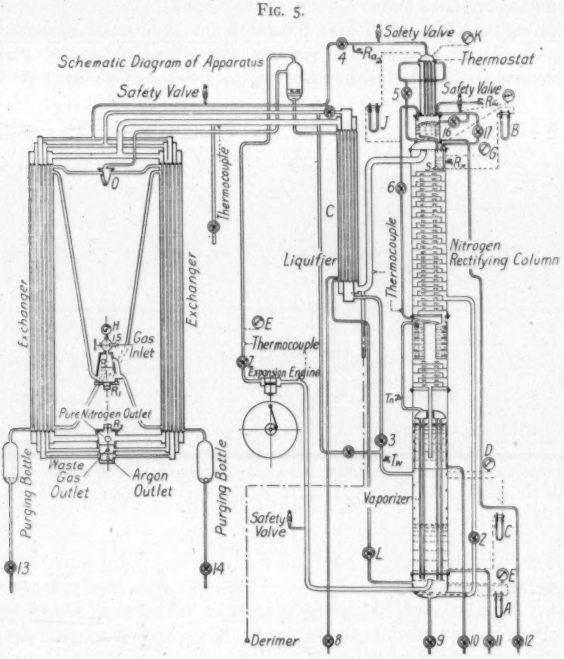


FIG. 4.

Schematic drawing of Plant 2, Port Worth, Texas.

At the time of the armistice 147,000 cubic feet of helium, averaging 93 per cent., was on the dock ready to be loaded for Europe. This gas had been obtained during the experimental work. Altogether about 200,000 cubic feet of helium was produced by Plants 1 and 2.

FIG. 5.



Schematic of Still and Interchanger, Plant 2, Fort Worth. During the war for purposes of secrecy helium was called "argon"; hence "argon outlet" on the schematic instead of "helium outlet."

Owing to the better results obtained by Plant 1, it was decided by the Army and Navy that a large production plant should be built based upon the equipment and operation of Plant 1. With this in mind, it was thought advisable to stop the experimental work in connection with Plants 1 and 2, and, therefore, on Jan-

uary 23, 1919, the two plants were shut down. A large production plant has since that time been slowly but steadily going up, and on January 1, 1921, was nearly ready to start regular operations. This plant involves an expenditure of about two million dollars for both buildings and equipment. It was constructed under direction of the Bureau of Yards and Docks and will be operated under supervision of the Bureau of Steam Engineering of the Navy. It consists of six units, five of which are operative, and one is to be retained as a spare. Each unit is designed to

FIG. 6.

General view of Plant 3 (Jefferies-Norton System). The plant is shown to the left; the gasolene absorption towers of the Lone Star Gas Company in the left foreground; and the living quarters to the right.

handle approximately 44,000 cubic feet of natural gas per hour, which gives an approximate total per day of five million cubic feet. Just what recovery the plant can obtain, of course, is not yet known, but if it obtains an average recovery of 60 per cent. on the helium, it will have, on the five million basis, a capacity of approximately thirty thousand cubic feet of 90 per cent. helium per day. It is hoped, however, that the grade of the final product can be raised to not only 93 per cent., but even 94 per cent., or a little better.

Plant 3 at Petrolia had many obstacles to overcome. Its location was poor from the transportation point of view, but it was thought that its location, close to the Lone Star Gas Company

compressor plant, would have many advantages. For experimental purposes, it was decided that it would not be necessary for Plant 3 to have its own complete compressor outfit, as it could get the gas from the Lone Star Compressor Station at from 225 to 250 pounds, and could then boost it with one compressor up to the operating pressure of 300 pounds. This arrangement eliminated a considerable amount of equipment at the start, and enabled the plant to get into operation a little earlier.

On the other hand, the apparent gains by this system were more than offset by difficulties which were not anticipated. Owing

FIG. 7.

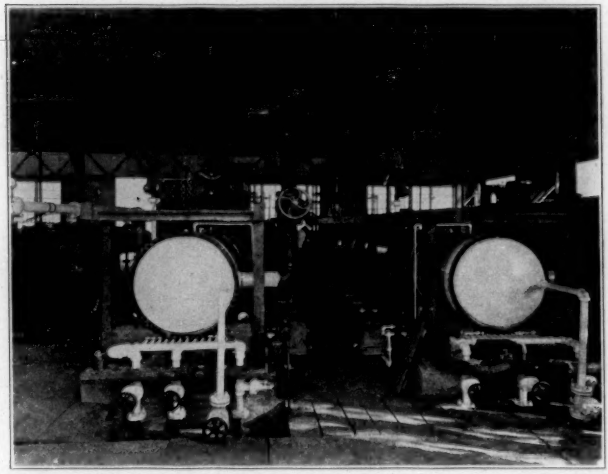
Compressors in Plant 3, Petrolia, Texas.

to the construction and operation of the Lone Star gasolene absorption plant frequent "slugs" of salt water and seal oil (used as an absorbent for the gasolene) were shot over to Plant 3 along with the gas, and on each occasion it was necessary to shut down the operations of the government plant. Notwithstanding these and other difficulties, a run was obtained on April 2, 1919, during which helium of a grade of 19.8 per cent. was produced. On April 17, 21 per cent. helium was made, but the plant has not been able to produce helium regularly and consistently, the above results being obtained on specially favorable runs. The Jefferies-Norton process was given an extremely difficult undertaking right at the start in applying it to the extraction of helium from natural

gas where there was less than one per cent. of the material to be extracted in the product used. In addition there was no intermediate experimental work done between a small laboratory equipment and the installation of Plant 3, which is probably the largest single refrigeration unit in the world. Under these circumstances the performance of the plant was quite remarkable.

Since the time mentioned a number of changes have been

FIG. 8.



Interior, Plant 3, Petrolia, Texas. This picture shows the two parallel interchangers before being covered with insulating material. The different sections are plainly shown. The two stills are seen in the rear centre, and the expansion engines on the left.

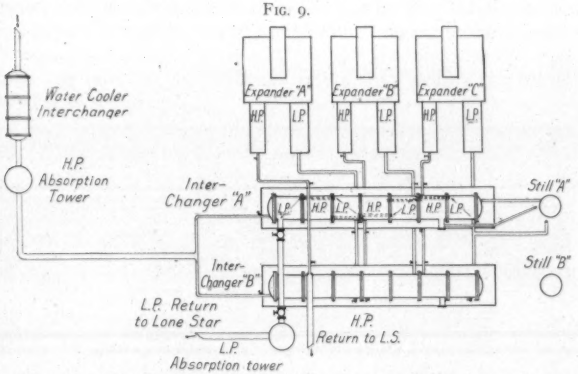
made in Plant 3, with the object of improving its operating efficiency. During the fall of 1920 some radical changes were made in the whole design of the plant, and these will probably be ready for testing out in February, 1921.

Theory of Refrigeration.—One way by which work can be measured is by the product of pressure and volume pv. It has been shown that for ordinary gases at constant temperature, pv is not quite constant. If air is taken as an example, the value of pv at 0° C. increases as the pressure falls, which gives rise to cooling

on expansion. In the case of hydrogen at the same temperature, the product pv decreases with fall of pressure, and, therefore, in the case of this gas slight heating takes place on expansion. There is, however, in the case of hydrogen a reversal at about $-200°$ C., and if the gas is pre-cooled below this temperature before expansion, a cooling effect instead of a heating effect is obtained.

In 1854 Joule and Thomson carried out some extremely interesting experiments, which showed that highly compressed gas (with the exception of hydrogen, and, as more lately ascertained, helium) when expanded through a porous diaphragm becomes

FIG. 9.



Schematic of Plant 3, Petrolia. There are two parallel interchangers with a still to each interchanger. The three expansion engines can be used either on one still and one interchanger or on both pairs so that the capacity can either be one and a half million cubic feet of raw gas per day or three million cubic feet.

decidedly cooler. This is due to the work which is done against molecular attraction. There is, therefore, in gases a cohesive force which increases with the density. If we were dealing with perfect gases, following exactly the laws of Gay-Lussac and Mariotte, the gases should not cool at all during expansion. Gases, however, are not perfect in this sense of the word, and a small cooling effect actually takes place, the effect being stronger the less perfect the gas is. The cooling "d" for air for a fall of pressure of $(p_1 - p_2)$ atmospheres is, according to a formula derived by Joule and Thomson: $d = 0.276\ (p_1 - p_2)\left(\frac{272}{T}\right)^2$ in which T is the absolute temperature of expansion.

From this formula it can be seen that the fall of temperature "d" depends on the fall of pressure. In addition the lower the temperature, the larger the temperature fall caused by expansion, since T becomes less.

If instead of expanding a compressed gas through an expansion valve, the gas is allowed to do work in an expansion engine which is practically nothing but a reversed compressor working against some external resistance, which may be either a brake or more commonly a small generator, we will find that the gas becomes cold very rapidly and parts of the expansion engine will become coated with frost. This method of cooling by means of adiabatic expansion in an engine with a piston is very efficient and is theoretically covered by the formula $\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{0.29}$.

FIG. 10.

New Helium Production Plant (Linde System), Fort Worth. The cooling pond is seen on the extreme left with a large number of cylinders piled in the rear. Of the two large buildings, the one on the left is the compressor building, and the one on the right the "process" building. The carbon dioxide removal towers are in the centre foreground, and the laboratory and office on the right.

The results obtained are much better than expansion through a nozzle except near the critical temperature of the gas, when the nozzle becomes nearly as efficient as the expansion engine. In order to get the necessary refrigeration with nozzle expansion it is necessary to go to very high pressures, whereas only moderate pressures are required with an expansion engine. The Linde system of refrigeration which was used by Plant 1, therefore, involved much higher pressures than the Claude system of refrigeration used by Plant 2, which used an expansion engine. This was the main difference in fundamental apparatus between the two plants, although the equipment varied considerably in detail.

In both plants the initial pressure to which the gas was compressed could not be maintained, as the gas in each case was

expanded from a higher pressure to a lower pressure when it entered the fractionating column or still.

In practice, in order to obtain the necessary temperatures, and in order to conserve power, and, therefore, costs, a heat interchanger is always used in connection with either system. This consists of a series of coiled copper tubes, one tube inside another with a counter flow of gases, the cold gas from the still going in one direction and cooling the warm fresh gas before it is fed either to the expansion valve or to the expansion engine. Sometimes the interchanger consists of a series of straight tubes placed very close together somewhat similar to a tubular boiler. The ideal condition to be aimed for is to have the temperature of the outgoing gas after passing through the interchanger practically the same as the temperature of the fresh gas entering the interchanger.

Since the liquefaction of the gas is dependent upon two factors, namely, its temperature and pressure, it is important to keep as high a pressure in the still as possible in order to be able to work at higher temperatures. On the other hand, if the expansion does not take place down to relatively low pressures a very considerable amount of refrigeration is lost, and the necessary temperatures are not attained. The Jefferies-Norton system, used by Plant 3 at Petrolia, gets around this difficulty by holding the initial pressure all through the interchanger and still. After the gas has passed through the still, it is expanded through a series of three expansion engines, and the exhaust gas from these engines goes into the outer sections of an interchanger of a tubular boiler type, thus cooling the incoming gas, which passes through the tubes themselves (see Fig. 9). By working the expansion engines at different temperatures, and thus liquefying the different hydrocarbons in the natural gas progressively instead of cooling everything down to the same temperature, additional efficiency is possible.

Plant No. 1. Helium Production Plant.—In so far as its essential features are concerned, the new helium production plant at Fort Worth is a duplicate on a larger scale of the original experimental plant, using the Linde system. The outline which follows is, therefore, a description of the new plant rather than the old one, although the process is practically identical.

The natural gas is first treated for the removal of carbon

dioxide, which is present in quantities varying from .2 to .3 per cent. This is done by bringing the gas under low pressure in contact with lime water in specially designed scrubbers in which the gas is sprayed with lime water for a sufficient length of time to reduce the carbon dioxide to the necessary maximum. The CO_2 removal system consists of five units, one of which is a spare. In each unit the incoming gas passes from the top of the scrubber to the bottom and comes in contact with a solution of slacked lime, which is sprayed into the tank by a series of nozzles near the top. The gas is then passed to the top of a similar scrubber in which it comes in contact with a fresh lime solution. The lime water flows from the scrubbers, is filtered and re-circulated. The natural gas freed from carbon dioxide passes under 3-inch water pressure to two 5000 cubic foot holders which act as reservoirs for the compressors. The heat of compression is removed in the usual way through intercoolers between each stage of compression and through aftercoolers in which the gas is cooled by circulating water.

In addition to the usual Linde method of obtaining low temperatures by means of nozzle expansion, a carbon dioxide cycle is also used as a gas forecooler. The compressed gas is led through this forecooler, in which most of the water vapor is removed by freezing. The cooled gas goes from the forecooler to the gas interchangers, where it meets the cold gas returning from the still. This returning gas precools the incoming gas to a temperature sufficiently low to give the desired effect after expansion. Arrangements are made in connection with these interchangers so that there is a progressive cooling first carried out by the returning vapors of the heavier hydrocarbons, and ending up with the return nitrogen, which is liquefied in the upper portion of the still. From the interchangers the gas is expanded through a nozzle into the still and enters the bottom of the still partly in the liquid and partly in the gaseous state. The still consists of three units, each unit being a rectification column, with a condenser at the top and a receiver at the lower end. The gas enters the lower unit and passes up through the middle unit, and thence to the top one. Each unit is so designed as to remove a definite portion of the constituents of the gas in the liquid state, and deliver a definite portion of the gas in a gaseous state to the next higher unit. A definite temperature gradient is maintained in

each unit and the constituents are progressively removed by liquefaction and re-evaporation and go back through the interchangers. In order to get a reasonably high grade product, such as 70 per cent. helium, it is necessary to liquefy the nitrogen in the gas as completely as possible. To do this, and not have the vapor pressure of the nitrogen too high, the upper unit of the still must be at the temperature of liquid nitrogen. In order to accomplish this a separate nitrogen cycle is used, in which pure nitrogen is liquefied and surrounds the condenser of the upper unit of the still. The make-up for this nitrogen cycle in the original experimental plant had to be purchased, but the new plant is designed to obtain the necessary make-up in the form of pure nitrogen from the operations of the plant itself, in which a sufficient amount of the nitrogen in the natural gas will be completely separated from the methane and other hydrocarbons.

The liquids collected in the receivers of each unit are used as required in the condensers of the middle and lower units. All outgoing gases from the still pass through the gas interchangers and gas forecoolers, thus precooling the incoming natural gas. These outgoing gases are mixed at the final outlet, and are returned to the mains which supply the cities of Dallas and Fort Worth. The gas, therefore, is simply robbed of its helium and a small portion of nitrogen, the rest of the gas being used for commercial heating and lighting purposes.[58]

Plant No. 2.—Fig. 4 represents a schematic of Plant No. 2 of the Air Reduction Company, using the Claude system. The natural gas is taken from the holder at atmospheric pressure, and led through a series of scrubbers, filled with hollow tile, over which caustic soda solution is circulated. The gas freed from carbon dioxide then goes through separators, in which a good deal of the moisture is eliminated, and from the separators to the compressor, in which the gas is compressed to 600 pounds. It then goes through a series of coolers, in which it is cooled to atmospheric temperature by water, and then through oil removers. It is then passed through a series of eight dryers, filled with porous calcium chloride. In the Claude system it is necessary to have a reasonably dry gas, owing to the fact that the tubes in the interchanger

[58] Owing to the contract between the government and the Linde Air Products Company, it is not possible to write a more detailed description of the equipment than is given.

are extremely small. After passing through the dryers the gas goes to the interchangers, where the incoming gas meets the cold gases coming back from the still in a similar manner to the Linde plant. Plant No. 2, however, made no use of a carbon dioxide cycle, and had no auxiliary refrigeration system. After going through the interchangers 25 per cent. of the gas is run through a liquefier, which is cooled by the returning gases from the still before these go to the interchangers. The other 75 per cent. of the gas is expanded through a small vertical expansion engine from the original 600 pounds pressure down to 120 pounds. This portion of the gas from the expansion engine, therefore, enters the bottom of the still containing some spray. Fig. 5 gives an outline of the arrangement of the still and interchangers. The liquid from the liquefier "C" drains into the bottom of the still and is led up to the rectifying column, from which it drops into the various compartments below, filling each compartment and overflowing to the one beneath. The gas coming from the expansion engine is partially liquefied in passing up through the tubes of the condensers, and finally reaches the top condenser, which is cooled by the expansion of a liquid consisting of a mixture of liquid nitrogen and methane. The last traces of the methane in the gas are practically all removed at this point, and also a considerable proportion of the nitrogen. The helium with the unliquefied nitrogen passes into the helium reservoir.

This plant was able to make helium, and to make it at times fairly consistently, but it could not deliver helium steadily, as the necessary temperatures could not be maintained at the top of the still, if the helium was allowed to flow out at a constant rate. Whereas the plant on the mechanical side could operate steadily, the helium could only be delivered periodically for the above reason.

Some changes in the column were made toward the end of the experimental period, but these changes did not improve the operating results.

Plant No. 3 (Jefferies-Norton system) was located at Petrolia, close to the compressor station of the Lone Star Gas Company. As already stated, this plant holds its initial pressure on the gas through the interchanger and still, and only expands the gas through an expansion engine after the gas has passed through the still. In this respect, it is different from the Claude system.

In addition there are three expansion engines working at different temperatures instead of one. In this way the hydrocarbons contained in the gas are liquefied progressively, and it is not necessary to reduce all of the gas to the same temperature. This increases efficiency and lowers operating costs. Fig. 9 is a diagrammatic sketch of the interchanger and still. The gas enters the interchanger at a pressure of 300 pounds, and passes through the tubes in the interchanger. There are seven sections in the interchanger, alternatively low pressure and high pressure, through which the inner high pressure tubes run. Each tube is ¾ inch in diameter, and baffles are placed against the tube sheets, causing the gas to travel a number of times backwards and forwards before it ultimately goes into the next section. The incoming gas, therefore, in going through the tubes traverses each section of the interchanger seven times before it goes into the next section, thus giving a high efficiency on heat interchange. The baffles placed between different sections cause the liquids which are formed in each section to fall to the bottom of the space between the tube sheets of adjacent interchanger sections where they can be drained out through proper drains, and can be expanded back into the outer low pressure sections of the interchanger at points where this expansion will give the best refrigerative effect. It was planned that all of the hydrocarbons would be successively liquefied in the first five sections, except the methane, which would come down in the last two sections, and be used for charging the still. The end of the interchanger, therefore, nearest to the still, would have to have a sufficiently low temperature to liquefy methane from a gas mixture at 300 pounds in order that the still could be charged, and the whole system could function properly. This liquid methane is then charged into the bottom of the still in the inner pot and is used for cooling the portions of the still higher up by expansion through needle valves into reflux coils placed at different points in the still. These coils are to reliquefy the gases coming up through the still through evaporation of liquids in the trays, so that there can be a constant fractionation in the column, the liquid in the trays liquefying the gases coming up through them having a higher boiling point, and they, themselves, evaporating, to be condensed higher up the still. The coils in the upper portion of the column are connected with a vacuum pump, so that liquid nitrogen which is produced at this point can be

boiled under reduced pressure, and a very high grade product obtained. It is hoped that this will eliminate the necessity for repurification and its attendant costs.

All gases except the helium and that portion of the condensed gas used in the still coils are re-evaporated back into the last high-pressure section of the interchanger. From this section a portion of the gas goes through No. 3 expansion engine, the expanded gas going into No. 7 low-pressure section of the interchanger, and this cold gas together with the expanded gas from the still coils gives the necessary refrigeration to liquefy the methane. In actual practice the exhaust on this engine has dropped as low as −155° C. to −160° C. All of the high-pressure sections are connected together by "jump tubes," so that the pressure in the three high-pressure sections is the same. Therefore, a part of the gas not used by expansion engine No. 3 is used by engine No. 2, which exhausts into low-pressure section No. 5. The residual gas is expanded through engine No. 1, which exhausts into section No. 3. This, therefore, gives a progressive cooling effect down the interchanger from the warm end to the cold, which results in the fractional liquefaction of the hydrocarbons.

One novel feature of the Jefferies-Norton system is the use of the power generated by the expansion engines. These engines are so connected as to assist the compressor in compressing the incoming gas so that they help to decrease the actual power used in compression.

As already stated, this plant has made helium for short periods containing as much as 21 per cent. of the rare element, but cannot be, at the present time, considered a commercial success, as it has not been able to operate steadily with the production of helium. Mechanically, however, it has done everything expected of it. Besides the troubles already referred to, due to its location, it has been extremely difficult to separate ethane from methane in the interchanger by a fractional liquefaction, as, owing to the low average percentage of ethane after passing the gasolene absorbers (2 to 3 per cent.), the partial pressure of this gas is quite low. At the time of writing some rather radical changes are being made in the plant, involving an auxiliary refrigeration system and a new still of the cascade type. Additional equipment has also been put in to protect the plant from variations in the operations of the Lone Star plant.

Repurification.—Plant No. 1 produced helium averaging about 70 per cent. in purity. The gas produced by Plant No. 2 averaged less than this. It was, therefore, necessary to refine this product up to a higher degree of purity in order to make it available for military and naval purposes.

Plant No. 1 is the only plant that did any experimental work on refining. The 70 per cent. helium which was stored in gas holders was compressed to about 1000 pounds, and passed through the helium forecooler and helium interchangers to a still consisting of a single unit similar to the units of which the regular still was built. The forecoolers and interchangers used on this repurification cycle were similar in number and design to the forecoolers and interchangers used on the regular gas cycle previously described. The one unit still consists of a rectifying column, having a condenser at the top and a receiver at the bottom. Liquid nitrogen was supplied to the outside of the condenser from a closed external nitrogen cycle. The impure helium was expanded into the bottom portion of this still, with the result that the nitrogen was condensed and the purified helium, in grade 92 to 93 per cent., was led from the top of the condenser. This helium as well as the waste nitrogen was used in the helium interchangers and forecoolers to precool the incoming impure gas. The purified helium was compressed to 2000 pounds pressure in cylinders, each cylinder holding 200 cubic feet at this pressure.

By this method it is probable that a gas containing not more than 93 per cent., or at the most 94 per cent., helium can be obtained unless the liquid nitrogen supplied to the condenser by means of the closed cycle is boiled under reduced pressure, in which case the temperature might be dropped below −200° C., with the result of a much higher grade product. This has not yet been done.

Another method of purification which gives promise of great usefulness is the one developed by the Bureau of Mines' helium laboratory at Fort Worth. This work was done by Dr. Leo Finkelstein and Mr. C. W. Seibel.

It was found that at the temperature of liquid air, charcoal was able to adsorb the nitrogen very efficiently, and at the same time had a selective action on this nitrogen, since the helium was adsorbed to only a very small extent. The following table

gives in a condensed form the main results obtained in connection with a certain charcoal, which is on the commercial market:

Temperature minus Cent.	c.cm. Helium ads. per gram charcoal.	c.cm. Nitrogen ads. per gram charcoal.	Per cent. ratio.
−190	6.5	302	2.15
−159	4.0	246	1.63
−104	0.85	121	0.70
− 86	0.45	92	0.49
− 75	0.30	70.8	0.42
− 48	0.20	48	0.415

The per cent. loss of helium is small and even the helium, which is adsorbed, can be pumped off by a vacuum pump without being contaminated with nitrogen.

The curve showing the grade produced is exceedingly interesting, as the point at which the curve breaks as regards purity is very sharp. The grade holds steadily at 100 per cent. up to the breaking point, at which point the purity drops rapidly. This condition is extremely convenient and satisfactory for repurification purposes.

The Army is constructing a repurification unit on two railroad cars. One will contain the power unit for generating the necessary current, and the other car will contain the compressors and the necessary refrigeration apparatus for repurification of helium from balloons and dirigibles, after the purity has dropped below the minimum of efficiency. These cars can be sent to any point where they may be needed, and should be extremely useful. A charcoal repurification unit is being designed by the Bureau of Mines, and will be installed in this car for the repurification of helium from dirigibles after use.

Plant Methods for Helium Analysis.—It was extremely important during the experimental work to get quick analyses on the helium content of products obtained in the plants. In order to do this the Air Reduction Company used the Edwards' balance,[59] and the Linde Company used a viscosimeter,[60] in which the gas to be tested was allowed to flow through a minute hole in a piece of platinum foil, the apparatus being calibrated against pure nitrogen. In this manner a determination could be obtained in two or three minutes, and was correct within one or two

[59] *Tech. Paper No. 89, Bur. Standards.*
[60] *Tech. Paper No. 94, Bur. Standards.*

per cent., provided the helium content was not below 20 or 25 per cent. The Bureau of Standards [61] has developed an automatic recording equipment based on the heat conductivity of gases which has been adapted to the helium plants with considerable success. This apparatus has been used at Plant 3, and will also be used in the large production plant, and an automatic record can be kept of the analysis of the helium produced from a still at all times. The accuracy of these methods all depends upon there being present two gases only. If a third gas, such as methane, is present, it naturally throws off the results very considerably. As, however, a gas containing as much as 70 per cent. helium has, as a rule, nitrogen only as an impurity, all these methods are applicable to the testing of helium of this purity.

Production Costs.—The cost of production of helium for Army and Navy purposes is vital in connection with an undertaking such as has been under way. The actual cost of extracting helium on a large scale can be estimated fairly accurately within certain limits. The two plants at Fort Worth had fairly satisfactory operating conditions up to October 1, 1918. At that time, owing to the increased demand for gas in Fort Worth and Dallas, it was necessary for the Lone Star Gas Company to take into their main pipe lines gas from other fields besides the Petrolia field. This reduced the average helium content below 0.5 per cent., and also caused a considerable variation in the hydrocarbon and nitrogen content. This put the plants at a serious disadvantage, and made it impossible to estimate costs under normal conditions. However, the month of September was a satisfactory month for Plant 1, since it ran steadily for 80 per cent. of the time. The actual cost during this month to produce helium of 70 per cent. average grade was $146 a thousand cubic feet, figured on the 100 per cent. helium basis. Of this amount $53.40 went toward the purchase of nitrogen for the "make-up" on the external nitrogen cycle. As the new production plant will make its own nitrogen for this "make-up" in the regular course of operations, this item can be entirely omitted, leaving $92.60. The cost of power in this estimate was figured at one cent per K. W. hour.

The recovery of helium during this month was only 45 per cent. of the helium in the gas. There is no doubt that owing to

[61] E. R. Weaver and others: *Jour. Ind. and Eng. Chem.*, **12**, p. 359, 1920.

the experience afterwards obtained that this recovery can be considerably increased. In addition, the capacity of the new production plant is a little over five million cubic feet of raw gas per day as against 700,000 cubic feet for the experimental plant. The difference in overhead and other operating expenses of each plant will be considerable, and should cut the cost of production to a very marked degree. The Bureau of Steam Engineering of the Navy Department estimate that the actual operating cost in the new plant will be $56 a thousand cubic feet of 92 per cent. helium. This does not take into account certain overhead charges and amortization of the plant. As an ordinary business proposition, it would, of course, be necessary to take these items into serious consideration. On the other hand, as an insurance against war, and as an insurance against the destruction of our cities by the dirigibles of other nations in case of war, the original investment in the helium experimental work and in the helium plants can well be written off the books by the nation.

If the Jefferies-Norton process proves to be a commercial success, helium can be manufactured more cheaply than the figure above mentioned. Taking into consideration the average operating costs of this plant, and assuming a recovery of 60 per cent. on the helium, it is possible that this plant may be able to produce helium at $20 a thousand cubic feet, figured on 100 per cent. basis. If the recovery is higher, the cost will be correspondingly lower. This figure, also, does not take into consideration amortization charges.

Professor J. C. McLennan [62] estimates that helium can be produced in his plant in Canada, if necessary changes are made, at less than $50 per thousand cubic feet. This does not include the cost of the gas. He does not, however, give any figures of actual costs to substantiate this statement, and the estimates are apparently based on an equipment which at present cannot produce more than one hundred thousand cubic feet of helium per year.

The costs mentioned above are probably high owing to the fact that helium after once used in a dirigible can be used again by reprocessing. The cost of repurification is not, of course, anything like the cost of original production.

[62] *Jour. Chem. Soc.*, July, 1920, p. 923.

HELIUM IN NATURAL GAS.

When it was determined, at the beginning of the war, to extract helium for balloons and dirigibles, Mr. G. A. Burrell, of the U. S. Bureau of Mines, had a number of samples of natural gas analyzed for helium, and was fortunate to quickly locate the Petrolia field as one of the best, if not the best, source of helium in the country. This field is located in the northern part of Clay County, Texas, sixteen miles northeast of Wichita Falls and seven miles south of Red River. The field is elliptical in shape, extending about four miles from northwest to southeast, and about three and a half miles from northeast to southwest. At the northwestern end of the field is the town of Petrolia, which is served by the Wichita Valley Railroad.

In 1909 the Lone Star Gas Company laid a 16-inch pipe-line from the field to Fort Worth and Dallas, and for about five years these cities, as well as Wichita Falls, and other smaller towns in the vicinity, were supplied entirely with Petrolia gas. In 1915–16 another line was laid from the Fox and Loco fields in southern Oklahoma direct to Dallas, and the compressor station at Petrolia was also connected north with the Keyes gas field in Cotton County, Oklahoma. The gases from both Keyes and Fox fields are very low in helium, and, therefore, it has been necessary to segregate the gas from the Petrolia field for the use of the government plants. This was accomplished in the fall of 1918 through payment by the government to the Lone Star Gas Company of one and a half million dollars, to limit the production of gas from the Petrolia field to a certain maximum per day. This was done with the idea of partly conserving the gas until such time as the government plants would be ready to operate. Notwithstanding this, at the present time, there is only a few years' supply of gas left in the Petrolia field. A separate pipe line has been lain from Petrolia to Fort Worth to serve the new production plant. A typical analysis of the Petrolia gas is as follows:

	Per cent.
Helium	.93
Carbon dioxide	.25
Oxygen	.54
Methane	56.85
Ethane and heavier hydrocarbons	10.30
Nitrogen	31.13
	100.

There is a variation in the composition of the gas from the different wells in the field, but all within the Petrolia field proper are high in helium. The above analysis is quite representative of the average gas before being treated for the removal of gasoline.

The limited life of the field was recognized two years ago, and, therefore, a survey of the whole country for sources of helium in natural gas was started by the U. S. Bureau of Mines. Director Manning asked the U. S. Geological Survey to assign a geologist to assist the Petroleum Division of the Bureau of Mines in this work. Mr. G. Sherburne Rogers was chosen by Director Smith, of the Survey, and worked most efficiently with the Petroleum Division of the Bureau. After two or three months' work, owing to other demands on the Bureau of Mines' men, Mr. Rogers did the main field work for the rest of the year, and the results he obtained as well as those of the Bureau of Mines' men are contained in a recent bulletin of the Geological Survey.[63] It is to be greatly regretted that this young geologist lost his life the next year while doing professional work in South America.

All analytical work in connection with this report was done by Bureau of Mines' men at the laboratory at Fort Worth, under the immediate direction of Mr. C. W. Seibel. The data obtained in this preliminary survey were not always complete, owing to the necessity for getting as much information in as short a time as possible. In July, 1919, the survey was continued by the Bureau of Mines, the writer being in general charge, the field force being directly under Mr. A. N. Dangerfield, and the laboratory at Fort Worth continuing under Mr. Seibel. About one thousand samples of natural gas have been analyzed for helium, and the larger proportion of these have also been analyzed for their other constituents. All data necessary for a complete appreciation of the commercial advantages of the different wells and fields have been collected, and will be published in due course of time.

During the period of this survey every natural gas field in the United States has been investigated, and the Bureau now has complete information regarding sources of helium in this country. One of the surprising things which has shown up in connection

[63] G. Sherburne Rogers: Helium Bearing Natural Gas, *Professional Paper No. 121, U. S. Geol. Sur.*, 1920.

with this survey is the large proportion of natural gases which carry helium in measurable amounts. Undoubtedly, over one million cubic feet of helium is being wasted in this country every twenty-four hours. The number of wells containing 0.2 per cent. or more is large. The number, however, which contain 0.5 per cent. or more is quite limited. In general, the richest gas is found in southeastern Kansas, in the Dexter, Sedan, and Augusta fields. These are the ones originally examined by Cady and McFarland, and some of the natural gases in these fields contain as much as 1½ per cent. helium, but the volume of gas is relatively small as the fields are old. However, it might be possible by a proper collecting system to obtain five or six million cubic feet a day or even more in these localities.

The state containing the largest number of helium gas wells is Oklahoma. The richest belt runs from southwest to northeast through the Osage country, and connects up with the wells in southeastern Kansas on the north, and with a considerable break connects with the Petrolia field on the southwest. Another break occurs between the Petrolia field and the east Texas field, where a considerable amount of gas carries as much as 0.2 per cent. or even 0.3 per cent. helium. The country in between the Petrolia and the east Texas field has not been drilled. The helium-bearing line strikes northeast through Kentucky and Ohio, where, in Vinton County, Ohio, a very considerable amount of gas, averaging between 0.4 per cent. and 0.5 per cent. helium, is available. In Pennsylvania, New York, West Virginia, Indiana, Kentucky, and Illinois, there is a considerable volume of gas containing from 0.1 per cent. to 0.3 per cent. helium. The western gases as a rule are barren, especially the large supplies of gas in Wyoming and California.

There is a curious relation between the proportions of helium and nitrogen present in natural gas. It is invariably true that helium is never found in natural gas that is not reasonably high in nitrogen. The converse, however, is not true, namely, that all high nitrogen gases contain helium. No definite relation can be established between these proportions, but helium is always accompanied by nitrogen.

The following table gives the analyses of a number of typical gases from different states which carry helium:

Table of Analyses of Natural Gases.

Laboratory No.	State.	County.	Field.	Depth.	Horizon.	Chemical Analyses.					
						Helium per cent.	CO_2	O_2	CH_4	C_2H_6	Residue N_2
274	Arkansas	Sebastian	Williams and Kiblev	....	Pipe Line Sample	.26	.00	.36	97.98	.00	1.40
A55	California	Fresno	Coalinga	....	.....	trace	....	....	....	....	....
362	Colorado	Rio Blanco	White River	530	Eocene, Wasatch Stage	trace	.15	.16	97.36	1.75	.58
525	Indiana	Randolph	Southwest	1093	Trenton	.23	.16	.48	73.49	16.86	8.78
142	Kansas	Butler	Augusta	1450–1500	Pennsylvanian	.50	.19	.57	74.74	12.92	11.08
168	Kansas	Chautauqua	Rogers	725	Pennsylvanian	1.28	.00	.83	54.20	.00	43.69
218	Kansas	Franklin	Peoria	719	Pennsylvanian	.17	.49	.71	98.55	.00	.08
198	Kansas	Montgomery	Big Bell	875	Stray sand above Oswego lime	.41	.08	.69	72.23	5.10	21.49
283	Kentucky	Floyd	Beaver Creek	1646	.....	.13	.16	.66	77.55	21.13	.37
179	Louisiana	Ouachita	Monroe	2163	Cretaceous, equivalent to Nacatoch	.18	.06	.67	98.02	.00	1.07
303	New York	Genesee	Pavilion	1900	Cretaceous Medina sand	.31	.00	.49	87.96	8.68	2.56
230	Oklahoma	Nowata	Ludowici-Celadon	687	Pennsylvanian	.04	.09	.66	96.54	.00	2.67
348	Oklahoma	Okmulgee	Henryetta	2210	Pennsylvanian	.14	.04	.57	78.19	18.43	2.63
135	Oklahoma	Osage	Pearson	777	Pennsylvanian	.63	.00	.45	59.33	.00	39.59
340	Pennsylvania	Green	Waynesburg	2807–2842	Bayard sand	.10	.00	.87	82.81	14.49	1.73
262	Tennessee	Scott	Glen Mary	1235	.....	.36	.18	.65	63.86	31.73	3.22
90	Texas	Clay	Petrolia	1713	Pennsylvanian "Cisco"	.90	.25	.54	56.85	10.33	31.13
88	Texas	Eastland	Eastland	1780	.....	.08	.00	.00	87.42	9.19	3.31
143	Texas	Stephens	Breckenridge	3099	.....	.21	.00	.12	76.48	19.68	13.50
510	West Virginia	Kanawha	Clendenin	1904	Squaw sand	.10	.32	.32	93.20	4.31	1.75
370	Wyoming	Niobrara	Lance Creek	....	.....	trace	.20	.63	69.06	29.19	.92

METHOD OF ANALYZING NATURAL GAS FOR HELIUM.

The method of Cady and McFarland[64] in their earlier work is still used with some modifications and gives excellent results. Two or three glass tubes, containing 20 grams of charcoal, are connected together by glass tubing, and arranged so that they can be readily heated to 300° C. by means of electric heaters, and the evolved gases completely pumped. When this condition is attained the tubes are immersed in liquid air, and at the temperature of liquid air the charcoal will adsorb nitrogen, hydrocarbons, and other heavy gases, but will not adsorb the helium, provided a sufficiently low vacuum is kept in the tubes. Stopcocks are placed between the charcoal tubes, and it is advisable to have a by-pass between alternative tubes, so that any particular tube can be eliminated from the train, if desired. The gas to be analyzed is run slowly through the train, the stopcocks giving the proper control, and everything but the helium is adsorbed. The latter gas is pumped by a sprengel pump into a graduated tube over mercury and the volume of the helium finally obtained is measured and corrected for pressure and temperature. The purity of the gas can be determined at any time during the analysis by observing the spectrum in a Plücker tube attached between the pump and the last charcoal tube.

Very concordant results can be obtained by this method and the work done up to date by the Bureau of Mines has indicated that the method is extremely satisfactory. If the pressure is allowed to build up too much, some helium is retained by the charcoal, but this is not true at the low pressures actually worked with.

ORIGIN OF HELIUM IN NATURAL GAS.

The origin of helium in natural gas is of great scientific interest. As already stated the origin of helium in the air is generally accepted as due to radioactive changes going on in uranium and thorium minerals in the earth's crust. The origin of helium in natural gas is more difficult to explain. The total amount of helium which has been evolved by the gas wells in the Petrolia field up to the present time is more than sixty million cubic feet. The area of this field is probably not more than eight or ten square miles, with a possible drainage area of forty to fifty square miles.

[64] *Am. Chem. Soc. Jour.*, Vol. 29, p. 1522.

It is inconceivable to the writer that sixty million cubic feet of helium could be produced by radioactive changes in the earth's crust within this limited area. Two thousand pounds of uranium metal, plus all of its disintegration products in equilibrium, will give 110 cubic millimetres of helium per annum. On this basis it is very easy to calculate how much uranium and what time would be required to give sixty million cubic feet.

Since the total volume of helium liberated in this country is probably as much as three to four hundred million cubic feet per annum, any argument for a radioactive origin has to assume large quantities of uranium or thorium minerals more or less localized. There is no evidence whatever of such deposits, and, therefore, such an explanation is at least unsatisfactory until we have more evidence of the presence of large deposits of radioactive minerals in the earth's crust.

Another explanation is that helium is more or less "primordial" in character, and, therefore, does not have anything to do with radioactive changes. Under this theory the helium might have been brought from the sun at the time the earth was thrown off from the sun. As explained in the early part of this article the chromosphere surrounding the sun consists of hydrogen and helium, and it might be possible for helium to be occluded below the earth's crust from such a source. One of the difficulties of this theory is to explain the more or less localized presence of helium. In addition, if helium in natural gas has such an origin, it should properly contain coronium and other gaseous elements which are known to exist in the sun, and helium derived from natural gas should be the most likely place to look for such new elements. The writer, with the assistance of Mr. Seibel, has already done some work in this connection. We have fractionated the helium obtained from natural gas by adsorption with charcoal under a pressure of 1200 pounds at the temperature of liquid air. Under this pressure, and at this temperature, there is a moderate adsorption of the helium, and this adsorbed helium was purified and a number of photographs made of the spectrum. There were no new lines found in this spectrum, but as it is probable that coronium is not only lighter than helium, but lighter than hydrogen, one would expect to get such a gas in the lighter fractions rather than in the heavier, and the work done up to date simply clears the way for a continuation, using charcoal as a means of

purification. The writer desires to express his cordial thanks to Professor Frost, of the Yerkes University, for his kindness in checking up the wave-lengths on one of the plates obtained.

The following gives the wave-lengths of unknown lines in the corona. In this table C stands for coronium, and P for proto-fluorine. The 5303.1 line in the green is the principal coronium line. Great care must be taken in attempting to recognize this line, owing to the fact that there is a secondary hydrogen line very close to it.

TABLE.

*Coronal Bright Lines. Campbell and Moore (1918).**

Mean λ.	Int.	Length minutes of arc.	All observers.		Nicholson's formulæ.
			Probable λ.	Int.	
.....	....	.....	3288?	Faint	P
.....	....	.....	28.2	Fairly strong	P
.....	....	.....	57	Faint	.....
.....	....	.....	88	Very strong	P
.....	....	.....	3455	Strong	P
.....	....	.....	61	Faint	.....
.....	....	.....	3505	Faint	P
.....	....	.....	34	Faint	C
3601.3	5	4½	3601.3	Pretty strong	P
.....	....	.....	26	Faint	P
41.4	2	1.3	41.4	Rather faint	.....
43.1	2	1.3	43.0	Rather faint	C
48.0	2	1.3	48	Rather faint	.....
** 51.8	1	.....	51?	Faint	.....
3801.4	1	2 ±	3801.0	Rather faint	P
.....	....	.....	65?	Faint	P
.....	....	.....	91	Faint	P
3986.9	1	2.5	3986.9	Fairly strong	P
4085.9	1	4 ±	4086.0	Fairly strong	P
.....	....	.....	4130	Faint	.....
4231.4	3	6	4231.4	Fairly strong	P
4240.8	1	3 ±	40.8	Faint	.....
44.8	1	3 ±	44.8	Faint	.....
.....	....	.....	4311	Faint	P
.....	....	.....	4359	Rather faint	C
**4397.4?	1	.....	98?	Very faint	P
4533.5	2	2 ±	4533.4	Faint	.....
** 67.4?	1	.....	67	Rather faint	C
.....	....	.....	86	Rather faint	P
.....	....	.....	4722?	Faint	P
.....	....	.....	25	Faint	P
**4778.6?	1	.....	79	Faint	.....
.....	....	.....	5073	Faint	P
.....	....	.....	5118	Faint	P
5303.0	10	4½	5303.1	Very strong	C
.....	....	.....	5536	Faint	P
.....	....	.....	6374.2	Strong	C

* *Pubs. A. S. P.*, 30, 350, 1918. ** Measured only by Moore.

If the two above explanations are not correct, it is necessary to accept more radical theories.

Rutherford has shown that if the velocity of the alpha particle drops below a certain minimum, the alpha particle will not ionize gases. This means that an element might be radioactive and give off alpha particles of low velocity, and our present methods of recognition of radioactivity would not be adequate to determine that the particular element in question was changing. The radioactivity of common elements, therefore, has been a question that has received some attention and some thought. Its importance has been accentuated by the presence of helium in certain non-radioactive minerals, and also the work of Strutt, who has shown, as pointed out in the early part of this article, that the Stassfurt potassium minerals contain helium in a quantity out of all proportion to the amount of radioactive material present. Are changes going on in nature about which we know nothing, and are these changes as radical and as important as radioactive changes about which we knew nothing twenty-five years ago? A study of the origin of helium in natural gas is of the greatest importance, as such a study may lead to something more than a mere geological discussion. All of the rare gases are found in some of the natural gases: argon, neon, krypton, and xenon are all present, although the percentages at present are uncertain.

COMMERCIAL STORAGE OF HELIUM.

From the financial standpoint the storage of helium is important. At the present time the government has at Fort Worth about one hundred thousand cylinders holding approximately 200 cubic feet each. The value of these cylinders is over two million dollars and the up-keep is considerable. Serious consideration of other methods of storage is, therefore, important.

It has been suggested by Mr. J. O. Lewis and Mr. G. S. Rice, of the Bureau of Mines, that helium might be stored after extraction in concrete chambers in mines. The suggestion is to build a concrete chamber in a drift, with reinforced concrete ends, and a manhole, the whole to be lined with sheet copper to prevent loss of the gas through the concrete. The gas would be stored under a pressure of 400 or 500 pounds, and the walls of the drift would take most of this pressure, so that the thickness of the

concrete would necessarily be small, and largely required for getting a smooth surface for the copper sheeting.

A good location probably would be in the St. Peter's sandstone in the Mississippi Valley, where the sandstone outcrops at the surface, and a long tunnel could be driven into the sandstone of the proper diameter and length. Under such conditions a chamber 400 or 500 feet long, and 6 or 8 feet in diameter, might be constructed and lined with copper or sheet lead. It is estimated that the cost of such storage per annum might be as low as from one-tenth to one-fifth of a cent per cubic foot.

It has also been suggested that helium might be stored in some of the salt deposits of New York. In this State some of the rock salt deposits are 60 feet thick and covered with a fairly heavy overburden. By drilling into the salt, and flushing out with a stream of water, a circular cavity could be made in the salt with a long neck, such cavity being 40 or 50 feet in diameter. The chamber would be something like a bottle with a very long neck, and helium might be stored in such a chamber under pressure satisfactorily. A series of "bottles" could be placed close together in the same deposit. It is necessary, of course, to know whether helium does or does not diffuse through salt in order to apply such a scheme practically, and this diffusion work is now being done by the Bureau of Mines.

The storage in a concrete chamber is being tried out at the experimental mine of the Pittsburgh Station of the Bureau, and it is expected that the practicability of this method can be determined shortly.

CRYOGENIC LABORATORY.

A very considerable amount of scientific data is still needed for the proper and efficient operation of the helium plants. Practically no work has been done in the past on vapor pressures, specific heats, or heats of vaporization of mixtures of helium, nitrogen, methane, and the other hydrocarbons, and yet the efficient operation of the plants is very largely dependent upon data of this character. This was recognized by the Bureau of Mines quite early, and some preliminary work was done at the Bureau of Standards by Messrs. Simpson and Osborne. Last year arrangements were made with Dr. Harvey N. Davis, of Harvard University, and Dr. F. G. Keyes, of Massachusetts Institute of

Technology, to do further work along this line, and this is now in progress. There is, however, a distinct advantage in having a thoroughly equipped laboratory which is available at all times for research work in connection with the plants, and this has been accomplished through the establishment this year in the Bureau of Mines at Washington of a cryogenic laboratory under the direction of the writer. Through the interest and broad-mindedness of Commander A. K. Atkins, of the Navy, and Colonel C. DeF. Chandler and Lieutenant R. S. Olmsted, of the Army Air Service, the necessary funds for the purchase of equipment and the present maintenance of this laboratory were furnished to the Bureau of Mines late last spring. The equipment is now being installed in the new Department of Interior Building at Washington. It consists of two 4-stage Norwalk compressors with a capacity of 75 cubic feet of free air per minute each. These will be used for making liquid air and for other purposes in connection with the experimental work. There will also be one vertical submarine type Norwalk compressor with a capacity of 12 cubic feet of free air per minute, to be used in connection with the liquid hydrogen cycle, and a similar compressor with a capacity of 8 cubic feet of free air per minute for use in connection with a liquid helium cycle. These compressors will all be driven by variable speed motors, and be equipped with unloading valves, so that the capacities can be varied within wide limits. In addition there will be an adequate equipment of gas holders, a machine shop, and a chemical and physical laboratory. The force will consist of Mr. J. W. Davis, mechanical engineer, of Yale and Stanford Universities; Mr. C. W. Seibel, physical chemist, of Kansas University; Dr. Leo Finkelstein, physical chemist, of the University of Chicago, and Dr. A. G. Loomis, physical chemist, of the University of Missouri. In addition, there will be an engineer and a mechanic available.

Whereas the main object of the laboratory will be to assist in every possible way the whole helium project, both on the production and refining ends, there is a strong desire that this laboratory shall be of material use to science in general, and that it may be possible later on to make arrangements for its facilities to be used in special cases by men outside the government service who are specially equipped for such work. There are a number of laboratories in the country that have liquid air machines. There

are three or four that have equipment for making liquid hydrogen, although up to date liquid hydrogen has only been made once or twice in this country in very small quantities. There is no laboratory outside of the one just described that has equipment for liquefying helium.

The writer desires to acknowledge the coöperation of the Army and Navy officials who have been connected with the helium work. A number of these have been mentioned in the course of this article. At the present time Lieutenant Commander Kraus represents the Navy and Major P. E. Van Nostrand the Army. Both of these gentlemen fully appreciate the importance of the work, and are bending every effort to make it a complete success.

Nitre Cake.—H. T. CALVERT and E. H. MORRIS describe the production and uses of nitre cake in Great Britain during the Great War (*Journal of the Society of Chemical Industry*, 1920, xxxix, Review, 408–411). Nitre cake is an acid sodium sulphate; it is produced in the nitre pots at sulphuric acid works, and in the retorts in which sodium nitrate and sulphuric acid are heated for the manufacture of nitric acid. Its acidity, calculated as sulphuric acid, may be as low as 28 per cent. or as high as 33 per cent., with an average of 30 per cent. During the war, the amount produced in nitre pots increased but 50 per cent. over the pre-war normal, while the amount produced in the manufacture of nitric acid increased 2000 per cent. The increased use of sulphuric acid for the manufacture of nitric acid for explosives greatly decreased the supply of the former acid available for industrial purposes. However, since large amounts of nitre cake were being produced, it was used in the arts in place of sulphuric acid. During the first ten months of 1918, the average monthly production of nitre cake was 27,500 tons, and the average monthly consumption 22,500 tons, or over 80 per cent. of the amount produced. Among the industries using nitre cake were: Grease recovery, bleaching and dyeing, metal pickling and cleaning, manufacture of hydrochloric acid, production of carbonated waters, glue, fertilizer, glass, alum manufacture, and some dozen other trade processes. In November, 1918, over 1000 railroad cars were in use for the transportation of nitre cake. The cake was drawn from the retorts into shallow cast-iron trays, permitted to solidify, and then broken into pieces of suitable size. Granulated nitre cake was obtained by rabbling the molten mass in rabbling pans, or by forcing a current of compressed air upon a falling stream of the molten mass, whereupon the nitre cake congealed as small pellets. Solutions of nitre cake in water were also placed on the market in carboys. J. S. H.

Foreign Zinc Industry in 1920. (*U. S. Geological Survey Note*, January, 1921.)—Of the European zinc-producing centres Belgium and Upper Silesia seem to be in the best condition. Belgium started the year with a smelter output of about 4500 short tons monthly, which it brought up by the middle of the year to 8000 tons. After that the output remained about stationary, so that the total production for the year was probably about 90,000 short tons. Reports near the end of the year indicate that the output is slackening and considerable stocks are on hand. The total stocks in Europe are thought to amount to 100,000 short tons. Belgian smelters have recently contracted for a supply of Australian zinc concentrates. The zinc output of smelters in Upper Silesia in 1919 was 81,596 short tons, equal to about 60 per cent. of the production in 1918. Reports for the first half of 1920 indicate a little larger production than in 1919, the output for the six months being 49,643 short tons. The zinc industry in other European countries and in Japan is reported at a low ebb. Perhaps the most noteworthy happening in the zinc industry during the year was the acquisition of the Mount Read and Roseberry mines, Tasmania, by the Electrolytic Zinc Co. of Australasia, by which that company gains immense reserves of ore. The enlargement of the electrolytic zinc plant at Risden, near Hobart, Tasmania, continues, a zinc rolling mill and a zinc oxide plant having been installed.

Positive Ray Analysis of Magnesium. A. G. DEMPSTER. (*Science*, December 10, 1920.)—It is not only in Europe that isotopes are being discovered by means of positive ray analysis. The announcement comes that in the Ryerson Physical Laboratory of the University of Chicago three isotopes of magnesium have been detected of atomic weights 24, 25, and 26, respectively. The rays from the 24 isotope are about six times as strong as the others, which are of equal intensity. This relation gives for the average atomic weight 24.375, which is not far from the accepted atomic weight 24.36.

The *Revue Générale des Sciences* for October 30, 1920, has an excellent article on this method of chemical analysis, written by Mlle. S. Veil.

G. F. S.

Improved Gunnery in the Navy. (*Scientific Am.*, December 11, 1920, p. 589.)—Analysis of the gunnery exercises of the American Navy during the past year shows that the greatest progress toward efficiency was made by vessels of the battleship class, due to the larger number of men aboard such ships and the comparative stability of the personnel. The Navy Department considers that battleship gunnery is at present about equal to that of foreign battleships. It is believed that next year vessels of other classes will be brought up as regards gunnery to the level of our battleships.

THE DETERMINATION OF THE STRUCTURE OF CRYSTALS.*

BY

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INTRODUCTION.

THE following discussion aims to give a brief survey of the field of the determination of the structures of crystals as it exists at the present time. The most essential events in the development of this work are mentioned, the existing means of experimentation are outlined, and some of its present limitations are discussed together with some of the kinds of problems to which a knowledge of the arrangement of the atoms in crystals has contributed and may be expected to contribute.

AN OUTLINE OF THE DEVELOPMENT OF THE MEANS EMPLOYED IN STUDYING THE STRUCTURES OF CRYSTALS.

The Experiment of Laue.—For some time it has been evident that the distance apart of the atoms in a solid body is of the order of 10^{-8} cm.[1] In the days before the nature of X-rays was known, attempts were made to see if they could be diffracted by passage through very narrow slits; the results of these experiments showed that if X-rays really were wave motions of a nature similar to ordinary light, their wave-lengths could not by much exceed 10^{-9} cm.[2]

Starting from this information Laue concluded that if X-rays are wave motions of this type they should be diffracted on passing through an orderly arrangement of atoms such as is furnished by a crystal; and, as a matter of fact, when a narrow pencil of X-rays was passed through a thin section of a crystal, a number of diffracted images of the pinhole defining the beam were obtained, arranged in a symmetrical fashion about an undiffracted

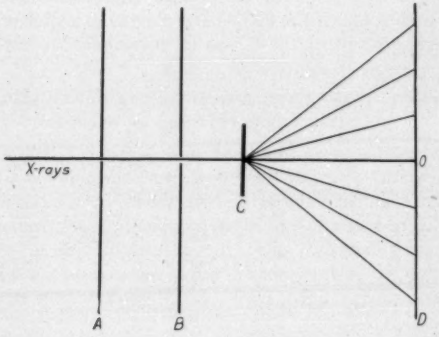
* Communicated by Dr. Arthur L. Day, Director of Laboratory, Associate Editor.

[1] An indication of the dimensions of the "spheres of influence" of atoms has been obtained in many ways, as from the thickness of soap-bubble films, from calculations based on the kinetic theory of gases, and more especially from the work of Perrin on the Brownian movement and from counts of α-particles.

[2] B. Walter u. R. Pohl: *Ann. d. Phys.*, **25**, 715, 1908; **29**, 331, 1908. R. Sommerfeld: *Ibid.*, **38**, 473, 1912. P. P. Koch: *Ibid.*, **38**, 507, 1912.

image.[3] The arrangement required for carrying out this experiment is shown in Fig. 1. A beam of X-rays after passing through two pinholes in the lead screens *A* and *B* proceeds through the thin section of a crystal at *C* and registers itself as the undeviated and diffracted images upon a photographic plate placed at *D*. The kind of diffraction patterns that are thus obtained are shown in Figs. 2 to 9.[4] Their symmetry is seen to be directly related to the symmetry of the diffracting crystal; for instance, the cubic crystal of magnesium oxide gives a fourfold pattern (Fig. 9) when the X-rays pass along a tetragonal axis, a trigonal crystal such as calcite furnishes a pattern (Fig. 7) that shows a three-

FIG. 1.



fold symmetry when the X-rays are travelling parallel to the principal axis.

The "Reflection" of X-rays.—In Laue's experiment the crystal may be thought of as behaving toward X-rays as if it were a three-dimensional diffraction grating. The mathematical treatment of such a grating [5] presents very considerable difficulties. Fortunately, however, W. L. Bragg has pointed out that these diffractions of X-rays by the atoms of crystals can just as satisfactorily, and vastly more simply, be treated as *reflections* from *planes of atoms* within the crystal.[6]

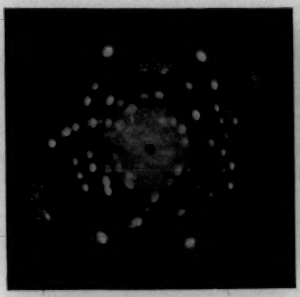
[3] M. Laue, W. Friedrich, u. P. Knipping: *Ann. d. Phys.*, 41, 971, 1913.

[4] Figs. 2 and 3 are obtained from photographs by F. Rinne, *Ber. Verh. K. Sächs. Ges. Wiss.*, 67, 303, 1913. The others have been prepared by the writer.

[5] M. Laue, W. Friedrich, u. P. Knipping: *Op. cit.*

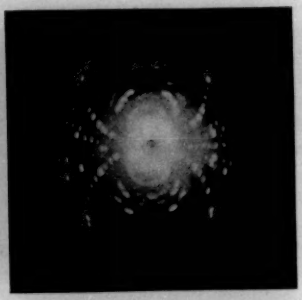
[6] W. L. Bragg: *Proc. Camb. Phil. Soc.*, 27, 43, 1913.

FIG. 2.



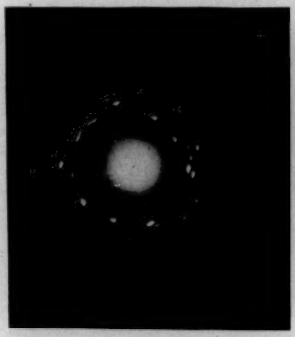
Cyanite. Triclinic. X-rays normal to the (100) face.

FIG. 3.



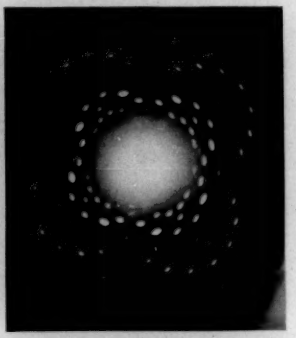
Skolezite. Monoclinic. X-rays normal to the (100) face.

FIG. 4.



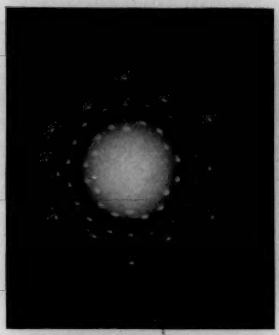
Potassium sulphate. Orthorhombic. X-rays normal to the (001) face.

FIG. 5.



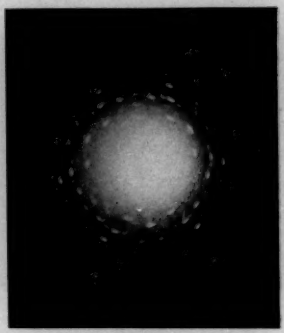
Rutile. Tetragonal. X-rays normal to the (001) face.

FIG. 6.



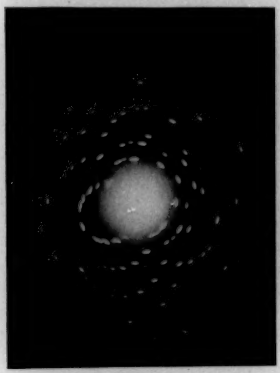
Carborundum twinned to give an hexagonal pattern. X-rays normal to the (0001) face.

FIG. 7.



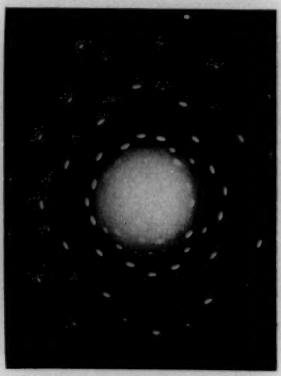
Calcite. Rhombohedral. X-rays normal to the base (111).

FIG. 8.



Calcite. Rhombohedral. X-rays normal to the cleavage (100) face.

FIG. 9.



Magnesium oxide. Cubic. X-rays normal to the cube (100) face.

This point of view suggests that X-rays ought to be "reflected" from the faces of crystals. If a parallel beam of X-rays of a single wave-length strikes the face of a crystal mounted at C (Fig. 10), it is found that X-rays are reflected at certain definite angles.[7] The mechanism of this "reflection" has an optical analogue: if a beam of light falls upon a stack of thin plates of transparent material such as glass, this light is found to be reflected strongly only at definite angles, the values of which will depend partly upon the wave-length of the incident light and the distance apart of the reflecting surfaces. These plates of glass may be taken as corresponding to the planes of atoms in the crystal.

The factors governing the reflection of X-rays can be shown with the aid of Fig. 11.[8] The reflecting planes of atoms parallel to a crystal face are represented by p, p_1 . . . p_n; the beam of X-rays A, A_1, . . . A_n strikes the face of the crystal at the angle θ; the distance between the planes of atoms is d. The following conditions will govern the reflection of the X-rays along the direction BC. Draw BE perpendicular to A_1B_1 and BD perpendicular to the planes p, p_1, . . . p_n. The difference in path between the ray ABC and A_1B_1C is

$$BB_1 - B_1E.$$

When this difference is exactly equal to a whole number of wave-lengths of the X-rays, the beam which is reflected from the plane p_1 will arrive at C exactly in phase with that reflected by the plane p; otherwise it will suffer practically complete neutralization by reason of the various sorts of phase relationships which exist between the reflections from the different planes of atoms. Consequently, in order that there may be a reflection of the X-rays along the direction BC, it is necessary that

$$BB_1 - B_1E = n\lambda,$$

where λ equals the wave-length of the X-rays and n (called the "order" of reflection) gives the number of whole wave-lengths difference in path of the reflected X-rays. In the triangle BB_1D the side BB_1 = the side B_1D so that $BB_1 - B_1E = ED$. Therefore,

$$ED = n\lambda.$$

[7] See W. H. and W. L. Bragg: "X-rays and Crystal Structure." London, 1918.

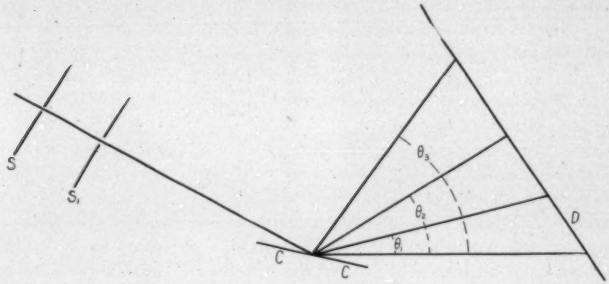
[8] W. H. and W. L. Bragg: *Op. cit.*, Chap. ii.

Now the angle DBE = the angle $ABp = \theta$; and $BD = 2d$. From this

$$ED = 2d \sin\theta = n\lambda. \quad (1)$$

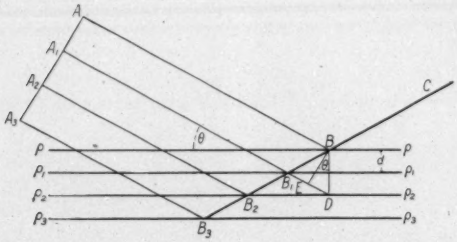
This is the fundamental equation underlying all reflections of X-rays.

FIG. 10.



Powder Reflections.—It has just been seen that diffraction, or "reflection," effects with X-rays result either from passing them through a thin section of a crystal (the Laue experiment) or by "reflecting" them from the face of a crystal. In both of

FIG. 11.



these cases a single crystal of considerable size and perfection is required. There is one other way in which definite diffraction can be obtained: by "reflecting" the X-rays from a haphazard arrangement of crystals such as is furnished by a fine powder.[9]

[9] P. Debye u. P. Scherrer: *Phys. Z.*, 17, 277, 1916. A. W. Hull: *Phys. Rev.* 10, 661, 1917.

In such a completely chaotic grouping of crystalline particles some of them will be in a position to reflect X-rays from each important crystal plane. Thus interference effects from all of the possible planes in the crystal will be produced at the same time. This third method of obtaining diffraction effects makes available for study the large group of substances which can not be obtained as crystals of appreciable size.

The Structure of Sodium Chloride.—The reflection of X-rays by crystals gives a means of obtaining information about the arrangement of the atoms in the crystal. If the structure of a crystal is known, then the wave-length of X-rays can be determined. From equation (1) it is seen that if X-rays of the same wave-length are employed, the relative distance apart of like planes of atoms in different directions can be derived from a measurement of the angles of reflection. From such measurements it appears that the spacings of like planes normal to the cube, dodecahedral and octahedral, (100), (110) and (111), planes of sodium chloride stand in the ratio of

$$1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}}.$$

W. H. and W. L. Bragg pointed out [10] that these observations can be accounted for if the atoms of sodium chloride have the positions shown in Fig. 22 (see page 223).

The Wave-lengths of X-rays.—A knowledge of the arrangement of the atoms in any crystal makes possible a determination of the absolute length of X-rays. The necessary procedure is somewhat as follows: A crystal may be imagined as made up of a vast number of units of structure, all alike in size and shape and similarly oriented; for instance a cubic crystal will be divisible into cubes, a hexagonal crystal into either hexagonal prisms or rhombohedrons, and so on. Fig 22 shows such a unit for the structure assumed for sodium chloride. That four chemical molecules are associated with this cube will be clear from the following considerations. The eight sodium atoms at the corners of the unit are each shared by eight cubes; all of them thus place within the unit the equivalent of the mass of a single sodium atom. The atoms N and P are each shared by two cubes; both together then supply another sodium atom within our cube. The two remaining sodium atoms are furnished by L and M and by Q and R. In a similar

[10] W. H. and W. L. Bragg: *Op. cit.*, Chap. vii.

fashion it can be shown that four chlorine atoms are associated with this unit.

The volume of the cube can be written:

where $$V = \frac{mM}{\rho}$$

V = the volume,

m, the number of molecules of sodium chloride within the unit, = 4,

ρ, the density of sodium chloride, = 2.17,

M, the mass of a single molecule of sodium chloride, equals the molecular weight multiplied by the weight of an atom of hydrogen, = $58.5 \times 1.64 \times 10^{-24}$ grams.

From these, d, the length of a side of the cube, $\sqrt[3]{V} = 5.60 \times 10^{-8}$ cm. If the reflection is taken from the face *CDHG*, then the distance d between like cube planes is the distance between the plane *CDHG* and the plane *BAEF*. The reflection from planes of such a spacing would be of the first order. But it will be seen that the plane *QLRM* has exactly the same composition as these other two planes and is spaced midway between them. The waves reflected from it will then be exactly out of phase with those from the other planes and, having the same amplitude, will blot them out completely. The first reflection to be found from the cube face of this arrangement of atoms is thus of the second order. If X-rays from a tube having a palladium target are used, the angle of this reflection is found to be 5.9°. In equation (1) we now have

$$n = 2,$$
$$d = 5.60 \times 10^{-8} \text{ cm},$$
$$\theta = 5.90°.$$

Consequently λ is equal to 0.576×10^{-8} cm.[11]

The obvious objection to this determination lies in the fact that though this particular structure for sodium chloride agrees with the experimental data just mentioned, there may be, for aught it tells, a myriad of other structures which are in equally good agreement. The large amount of data, however, agreeing with this structure and the value of the wave-length of X-rays derived from it that has since been obtained from different sources makes their truth seem highly probable.

Using this same method of procedure, W. H. and W. L. Bragg and others have found structures which will account for the positions of the reflections from the most important faces of a

[11] W. H. and W. L. Bragg: *Op. cit.*, Chap. vii.

number of crystals, such as sodium and potassium chlorides, iron pyrites, the diamond, carborundum, and various members of the calcite group of minerals.[12] Probably in no case can the structures which are *thus* obtained be said with absolute surety to correspond with the arrangements of the atoms within these crystals.

The General Method of Studying the Structure of Crystals.—It consequently becomes necessary, if we are to make any definite and certain progress toward unravelling the structures of crystalline compounds, that a method be developed which will make it possible to determine *uniquely* such structures, or at least that will indicate the degree of probability with which a particular structure has been determined. Fortunately the basis for such a method was already prepared, for the geometrical theory of space groups developed many years ago by Federov, Schönflies, and Barlow can be made to give *all* of the possible ways of arranging points in space so that the grouping which results will exhibit crystallographic symmetry.[13] Since a crystal is an orderly arrangement of atoms in space, it must correspond with one of these space groups. Consequently when the space groups are given a suitable analytical representation, a means quite independent of any X-ray experiments is provided for writing down *all* of the possible positions which the atoms of *any* compound can occupy. After this has been done the particular data which will serve to distinguish between these various possible arrangements can be selected and those methods of experimentation employed which will yield most readily the needed facts. Such a method has the advantage of being equally applicable to complicated and to very simple structures. The point of view involving such a use of the theory of space groups was used first by Nishikawa in studying spinel.[14] The geometry of the method arising from it, which has been in the course of development for several years,[15] may now be said to be nearly completely developed.

[12] W. H. and W. L. Bragg: *Op. cit.*, Chaps. vii and viii. C. L. Burdick and E. A. Owen: *J. Am. Chem. Soc.*, **40**, 1749, 1918; C. L. Burdick and J. H. Ellis: *Ibid.*, **39**, 2518 (1917); R. G. Dickinson: *Ibid.*, **42**, 85 (1920); and others.

[13] E. Federov: *Z. Kryst.*, **24**, 209, 1895. A. Schönflies: "Krystallsysteme u. Krystallstruktur" (1891). W. Barlow: *Z. Kryst.*, **23**, 1, 1894.

[14] S. Nishikawa: *Proc. Tokyo Math. Phys. Soc.*, **8**, 199, 1915.

[15] This development has been going on independently in Germany and in this country. For instance, see P. Niggli: "Geometrische Krystallographie des Discontinuums" (1919); Ralph W. G. Wyckoff, *J. Am. Chem. Soc.*, **42**, 1100, 1920; *Am. J. Sci.*, **50**, 317, 1920; *Ibid.*, **1**, 127, 1921.

THE METHODS OF OBTAINING DIFFRACTION EFFECTS FROM CRYSTALS.

The Spectrometer Method.—Three ways of obtaining definite X-ray diffractions have been mentioned: (1) by reflecting X-rays from individual faces of a crystal; (2) by reflecting them from a crystalline powder so that all of the possible crystal planes have an equal chance to reflect; (3) by passing X-rays through a thin section of a crystal. We shall now discuss very briefly the way in which these three kinds of experiments are carried out and point out the kinds of data that can be obtained from each.

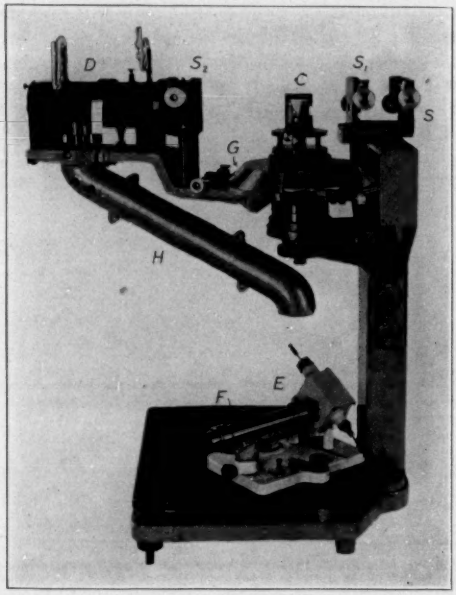
The first of these diffraction methods may be called the spectrometer method. X-rays, preferably of a single wave-length, are passed through two narrow slits of an X-ray spectrometer in order to render them parallel; this beam, after reflection from the face of a crystal mounted upon the spectrometer table, passes into an ionization chamber, where its intensity is measured by the magnitude of the ionization which it produces in the gas of this chamber. Such an X-ray spectrometer is shown in Fig. 12. The X-rays passing from an X-ray tube through the slits S and S_1 strike the face of the crystal mounted at C. When the ionization chamber D and the crystal C stand at the proper angles, the reflected beam of X-rays enters the chamber D through a mica window by way of the slit S_2. This chamber is filled with some gas, usually sulphur dioxide or, better, methyl bromide, which ionizes strongly under the action of X-rays.

The case of the ionization chamber is charged to a potential of about 200 volts, while the inside insulated electrode, which is connected only with the gold leaf of a sensitive electroscope E, is, at the moment of beginning the experiment, at the potential of the ground. As X-rays enter the chamber and ionize the gas within it, the potential of the gold leaf will change. The rate of this change is measured by the drift of the gold leaf and taken as an indication of the intensity of the reflected X-rays. By properly adjusting the positions of the crystal and of the ionization chamber, the relative intensities of reflection from a single face can be obtained for the various orders. This information is usually sought for several faces of a crystal.

In place of an ionization chamber and electroscope for measuring the diffracted X-rays a photographic plate can be used. If the X-rays are of a single wave-length an image of the slit will appear at the position conditioned by equation (1). If the X-rays in the

original beam are of more than one wave-length, as is usually the case, then for a perfectly constructed crystal—meaning thereby one in which the atoms are arranged with perfect regularity throughout the entire mass—and for perfectly parallel X-rays, only the image corresponding to one wave-length will appear upon the photographic plate for a particular orientation of the crystal.

FIG. 12.

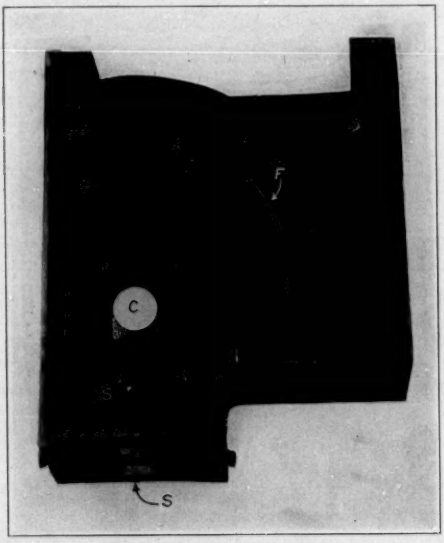


An X-ray spectrometer. *G* is a divided circle upon which the positions of the crystal and ionization chamber may be read; *F* is a microscope and scale for following the gold leaf of the electroscope (*E*); *H* is an earthed shield for the wire connecting the chamber and the electroscope.

If the beam of X-rays is slightly divergent after passing through the slit of the spectrometer, it can be shown from geometrical considerations that the X-rays of somewhat different wave-lengths which can thus be reflected will focus upon a surface which is as far from the crystal as the crystal is distant from the slit. This

fact is of utmost importance in designing an X-ray spectrograph. If a photographic film is curved to the arc of a circle of a radius equal to the distance from the crystal to the slit, and whose centre is at the crystal face, then a focused image of a small range of wave-lengths will appear upon the film. Furthermore, if the crystal is but rotated continuously back and forth, all of the

FIG. 13.



The front slit (s) is variable. The second one (s') is fixed at a considerable width so that the beam of X-rays striking the crystal mounted on the rotating table (C) is somewhat divergent. The photographic film is curved to the arc of a circle along F.

different wave-lengths in the original beam will be reflected at some angle of the rotating crystal. A photographic image of the entire X-ray spectrum can thus be obtained. Fig. 13 shows a spectrograph designed for obtaining such reflections. Fig. 15 (page 215) gives the X-ray spectrum of tungsten obtained in the manner just outlined.

Spectrometer Data.—The principal use of the photographic

X-ray spectrometer (spectrograph) in studying the structure of crystals lies in determining the absolute distances apart of like planes in some one direction in the crystal. This information, furnishing a knowledge of the number of molecules to be associated with the unit of structure, is the first piece of experimental data that is required in studying the structure of a crystal. It can be obtained much more readily by photographic means than by searching about looking for a reflection, as must be done if the spectrometer itself is employed to give the same information.

The following is an outline of the nature of the data which the spectrometer and the spectrograph can be expected to yield. It has just been stated that the number of chemical molecules associated with the unit of structure can be deduced from a knowledge of the position of the reflection from a single face of a crystal. The procedure required to give this information is quite the same as that already used in getting the wave-lengths of X-rays. Equation (1), $n\lambda = 2d \sin\theta$ can be written: $d = \frac{n\lambda}{2 \sin\theta}$. It has been indicated that

$$V = \frac{mM}{\rho}. \qquad (2)$$

$$V = c(d_{100})^3 \qquad (3)$$

where d_{100} is the spacing in the direction of the side of the unit prism and c is a constant whose value is determined by the symmetry of the crystal (and is obviously equal to unity in the case of a cubic crystal). By combining (2) and (3): $m = \frac{c(d_{100})^3 \rho}{M}$; substituting the value of d obtained by equation (1), there results:

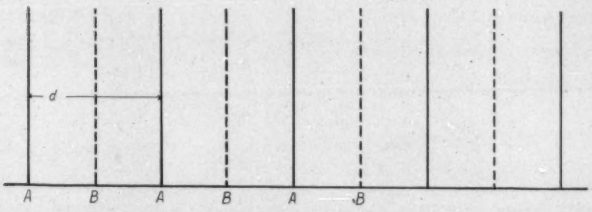
$$\frac{m}{n^3} = \frac{c\lambda^3 \rho}{8 \sin^3\theta M}.$$

Besides telling the absolute distances apart of the planes of atoms in the crystal, spectrometer measurements give some indication of the composition of these planes. Imagine that the atoms of a certain crystal are so arranged that in a direction normal to some face they lie in planes spaced as in Fig. 14. The distance apart of like planes of these atoms is d; but midway between the planes made up of atoms of A are planes of atoms of B. The waves reflected from the A planes and from the B planes will interfere to an extent which depends upon the relative reflecting

powers of these atoms. If, for example, the reflecting power of atom *A* were just equal to that of atom *B*, it is then quite clear that the first order reflection from one kind of plane, being of exactly opposite phase to that from the other, would just nullify the reflection from this other plane so that the distance apart of like planes would seem to be half of what it really is. If the reflecting powers of the two atoms were not equal, then there would still appear a first order reflection, but one weakened to an extent dependent upon the difference in the scattering powers of the two kinds of atoms.

The "Laws" of Reflection.—The use of this kind of information in deciding the arrangement of atoms in a compound necessitates that the relative reflecting powers for X-rays of the

FIG. 14.



different atoms be known. Previous studies of their scattering powers made it appear that atoms scatter and reflect X-rays in an amount very roughly proportional to their atomic weights, or, more correctly perhaps, their atomic numbers. The reflections from various crystals seem to have confirmed this rough proportionality; but whether the "reflecting" power is strictly proportional to the number of electrons in the atoms, and if not, what may be the exact nature of the function expressing their scattering powers, is at present unknown.

It has been stated that the use of the spectrometer makes possible the estimation of the relative intensities of the reflections from various crystal faces in the different orders. We have already seen how the intensity of reflection can be taken as an indication of the composition of the reflecting planes. But in order to do this it is obviously necessary to know the normal distribution of intensity in the different orders, or, what amounts to the same thing, to

know how the intensity of reflection depends upon the spacing between like planes of atoms in a crystal. The form of this function is not known now with any degree of certainty.

Until a knowledge of these two factors governing the amount of reflection of X-rays—the effect of atomic number and the effect of spacing—is available, it is useless to attack by the means we have been discussing any but the simplest of crystals. Even with these it is never certain that the structure selected as agreeing with the experimental data is actually the correct one. It may be urged that if a lack of knowledge of these two "laws" of reflection is the only thing that delays the determination of the structures of many and complicated crystals, then we should immediately proceed to discover the forms of these two expressions. The reason for not carrying out this apparently simple program is not hard to find. The commonly employed spectrometer method of studying the structure of crystals involves the simultaneous use of these "unknowns"; only in relatively few instances has it been possible to get at the arrangement of the atoms in a compound without assuming values for both of these expressions. Since it is only by working with crystals whose structures are known with certainty that progress can be made toward a satisfactory solution of these two problems, and since a use of the answers to these same problems are usually involved in getting the structures themselves, advancement has not been made.

These two "laws" which we have been discussing are of very considerable importance quite aside from their use in the determination of the structure of crystals. Such meagre information as is at present available seems to show conclusively that the forms they will take can only be accounted for by taking into consideration the intimate structure of the atoms themselves.

The diffraction or reflection of X-rays by an atom may be roughly pictured as follows: When a beam of X-rays of definite wave-length strikes an atom the rays may be supposed to accelerate the electrons contained within this atom. X-rays which are emitted by such electrons are the diffracted (scattered or reflected) radiation. If all of the electrons in an atom were concentrated very close to the centre the amount of scattered X-rays should be quite closely proportional to the number of electrons in the atom. Such a proportionality is in reality only very roughly fulfilled; in fact, some of the evidence seems to point to quite marked variations

from it. This lack of proportionality is most simply and easily explained by supposing that the atom, meaning thereby the volume occupied by the electrons surrounding the atomic nucleus, is relatively large. The X-rays scattered by electrons on one side of the atom will interfere, sometimes destructively and sometimes constructively—depending upon the absolute magnitude of the atom itself and upon the wave-length of the X-rays—with those rays scattered by electrons on the opposite side of the atom. This idea of atoms of appreciable size almost certainly must be called into play in order to account for the peculiar way in which the intensity of reflection varies with the angle of reflection.

This field of studying the intimate structure of the atom is quite untouched at the present time. The results which are to be obtained from it are, as we have seen, of more or less doubtful value until the determination of the structure of crystals has been put upon a very certain basis. When this has been done, that is, when we have succeeded in determining *uniquely* the structures of a few crystals, these methods of X-ray experimentation can quite properly be expected to yield very useful information.

The Method of Powders.—The *second* method of obtaining diffraction effects from crystals (the method of powders), is in a sense a generalization of the one just discussed. If a parallel beam of monochromatic X-rays is caused to fall upon a fine crystalline powder put in place of the crystal at *C* of Fig. 10 (page 204), a number of images of the slit produced by different planes of atoms of the crystal will be obtained upon the photographic plate at *D*. For instance, if the powder is that of a cubic crystal, some of the particles of this powder will have the orientation necessary for reflection from, let us say, the cube face, others for reflection from the octahedral face, still others from the dodecahedral face, and so on: consequently, images from each of these planes will appear upon the film. The kind of photograph that is obtained in this way is shown in Figs. 16 to 19.[19]

The information supplied by a powder photograph is about the same as that obtained by spectrometer measurements, except that now a single experiment furnishes a large number of reflections which in the other case would have to be made upon each face separately. This is obviously a great advantage. The pro-

[19] Figs. 16 and 17 are given by A. W. Hull, *Op. cit.;* Figs. 18 and 19 by H. Bohlin, *Ann. d. Phys.*, 51, 421, 1920.

FIG. 15.

The X-ray spectrum of tungsten using sodium chloride (cube face) as a grating.

FIG. 16.

The powder spectrogram from powdered silicon.

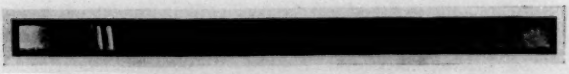
FIG. 17.

The powder spectrogram from diamond.

FIG. 18.

The powder spectrogram from nickel.

FIG. 19.



The powder spectrogram from magnesium.

cedure at the same time has several serious disadvantages, however: (1) it is greatly to be doubted if the photometered intensities of reflection, such as are to be obtained from these photographs, are at the present time as accurate as are the results derived from the use of the ionization chamber; (2) the amount of material which is reflecting X-rays in the formation of any one of these images is extremely small, so that relatively very long exposures are required; (3) partly because of this small amount of diffracted energy, the images are of considerable width, so that planes having about the same relative spacings—which are at present the most useful in studying the structure of crystals—will give effects which overlap one another; (4) used by itself this method fails to identify the reflection of any plane with a particular image. While this last objection is not serious when we are dealing with very simple compounds, it is exceedingly important for all of the more complicated cases.

The great use of this method lies in its opening up for study a vast number of chemical compounds which do not crystallize well. At present it is not known whether the atoms of many kinds of substances are arranged in an orderly fashion or not. For instance, are the individual particles of a colloidal substance in reality extraordinarily minute crystals, or are they more properly to be looked upon as more or less haphazard agglomerations of atoms? Or, are many of the naturally occurring minerals, such as chalcedony or the opal, perfectly disordered groupings of atoms, or are they built up of the minutest crystals which stand in disordered relations to one another? This method of obtaining diffraction effects may be expected to answer such questions as these. This field is, however, thus far practically unexplored.[17] Further, are liquid crystals crystalline in the sense that they are made up of a regular arrangement of atoms in space? We have here a method of attack for deciding it. If the atoms within the *molecules* of complicated organic compounds stand in a definite orientation to one another, then such compounds should give diffraction effects *even in the liquid state*. Debye and Scherrer[18] believe that they have obtained diffractions from *liquid benzine* which prove the existence of the benzine ring; in fact, it is said to be 6.02×10^{-8} cm. on an edge and 1.19×10^{-8} cm. thick. This

[17] See, however, S. Kyropoulos: *Zeit. anorg. Chem.*, 99, 197, 1917.

[18] P. Debye u. P. Scherrer: *Nach. Kgl. Ges. Göttingen*, December 17, 1915.

same method finds its use even in the field of chemical analysis.[19] Suppose that we have a substance which on solution gives a test for, let us say, sodium and potassium, chlorine and iodine. Is it a mixture of sodium chloride and potassium iodide, or is it a mixture of sodium iodide and potassium chloride, or are all four present together? The method we have been discussing will decide it, for each of the substances is characterized by its own distance between atoms, and once the pattern of images which each of these substances furnishes is known, it is only necessary to search for these same patterns in the photograph obtained from the mixture to be analyzed.

The Method of Laue Photographs.—The *third* method of obtaining diffraction effects from crystals is the original method of Laue. In this instance X-rays are passed through thin sections of individual crystals in a direction normal or nearly normal to some important crystal face. In this way reflections from a relatively enormous number of different crystal planes are obtained at one time. Some Laue photographs have been prepared which show nearly a thousand reflections; it is very common that the number should lie around three to four hundred. Of course several of these spots may belong to the same crystal form, but in spite of this fact the number of different kinds of planes that give reflections in a single photograph is very large.

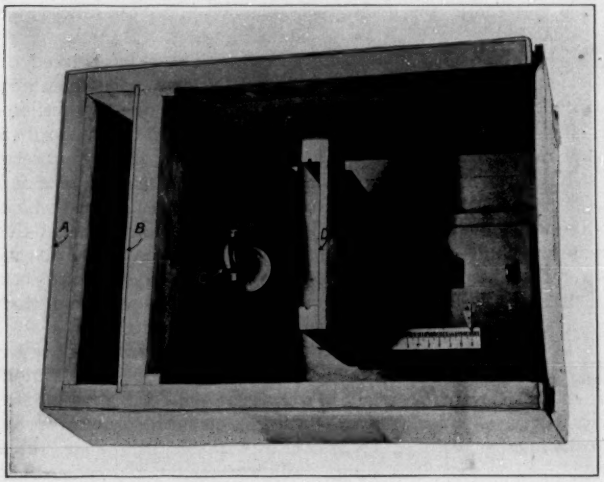
In contrast with the method of powders the principal use of the *transmission method* lies in its application to the determination of the structures of crystals. A study of the Laue photographs from a crystal, when combined with a spectrometer determination of the number of molecules associated with the unit of structure, supplies more data for distinguishing between the various possible arrangements of its atoms than does any other single method. Transmission photographs are of particular use at the present time because the relatively large amount of data which they furnish makes it possible to dispense to a large extent with the assumptions concerning the reflecting powers of the atoms and the effect of spacing upon the intensity of reflection. As already pointed out, unless some entirely new procedure is devised, it is only by taking advantage of the relatively few and scattering instances where structures can be investigated without the help of both of these two "laws" that direct progress can be made. It remains

[19] A. W. Hull: *J. Am. Chem. Soc.*, 41, 1168, 1919.

to be seen whether the Laue photographs will continue to give the most usable information after the forms of these two "laws" have been determined.

Whereas the other two methods employ X-rays of a single wave-length, the Laue photographs are obtained by the diffraction of that part of the radiation from an X-ray tube which, by reason of its analogy to white light, is called the "white radiation."

FIG. 20.



A form of the apparatus required for the preparation of Laue photographs. *A* and *B* are pinhole lead slits; the crystal holder *C* permits setting the section of the crystal at any desired orientation; *D* is a movable plate holder. Other and more complicated forms have been used; this one is desirable chiefly because of its simplicity.

Fig. 15 shows the spectrum of tungsten. Spectrometer measurements make use of the line radiation, the characteristic radiation; the Laue photographs are produced by the continuous portion of much shorter wave-lengths. This is alike an advantage and a disadvantage: a disadvantage because we must devise methods of studying the Laue photographs which will permit the determination of the wave-length; an advantage (1) because the wide range of wave-lengths that are available permit reflections from

a large number of planes for a definite setting of the crystal, and (2) because the shortness of the wave-lengths makes it possible for planes with very small spacings—and complicated indices—to give reflections that can be readily studied.

Fig. 9 (page 202) shows the Laue photograph that is obtained by passing X-rays through a thin section of magnesium oxide cut, or cleaved, parallel to the cube, (100), face.[20] In Fig. 1 (page 200) the pinhole beam of X-rays strikes this thin section of the crystal mounted at *C;* most of it passes directly through the crystal and forms an undiffracted image of the pinholes at *O;* the rest of the rays are "reflected" by the various planes of atoms in the crystal and produce a group of images, each one corresponding to a crystal plane, arranged about this central spot (Fig. 20).

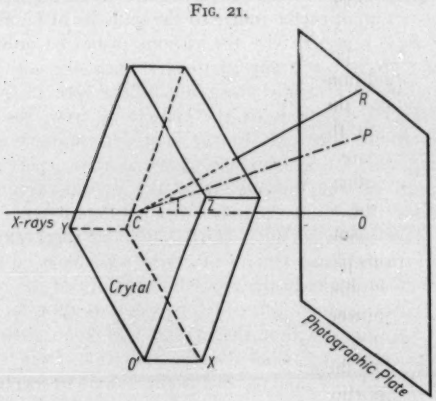
The relative positions of the reflections from the different planes are conditioned only by the kind of symmetry which the crystal exhibits; the absolute positions of these spots upon the plate depend on the distance from the crystal section to the photographic plate. The patterns from different cubic crystals, or from two other crystals which have the same axial ratios and belong to the same system of crystal symmetry, differ from each other then simply in the relative intensities of the reflections from the various planes; this of course depends upon the arrangement of the atoms within the crystal and upon their relative "reflecting" powers. Consider the reflection from the plane containing the line *CP* and parallel to the *Y* axis of a cubic crystal (Fig. 21). The intercepts of this plane upon the *Z* and *X* axes are in the proportion of 1 : 2; the *Y* intercept is infinity. Since the ratio of the intercepts of the plane are thus $2 : \infty : 1$, its indices must by definition be 102 ($\frac{1}{2}$, 0, 1). If the angle between this plane and the incident rays is θ, the reflection will be along *CR*, where the angle $RCO = 2\theta$. In a similar fashion the position of the reflection from any plane can be determined from the characteristics of symmetry of the diffracting crystal. Conversely, it is possible to get such characteristics as the axial ratio of a crystal from a study of the Laue photographs.

This purely geometrical problem of identifying the reflections that are obtained upon the photographic plate with those planes that may be thought of as producing them, can be easily solved with the aid of methods of projection familiar to the crystallogra-

[20] Ralph W. G. Wyckoff: *Am. J. Sci.*, 1, 138.

pher. Likewise the distance between like planes in terms of the indices of these planes for each of the units of structure which underlie crystals can be obtained from geometrical considerations alone. Furthermore the distance from the crystal to the photographic plate and the distance of a reflection from the central spot give the angle of its reflection. Then with the aid of expression (1) it is possible to get a value for $n\lambda$, the product of the order of the reflection into the wave-length of the reflected

FIG. 21.



X-rays, after one of the absolute dimensions in the crystal has been obtained from an X-ray spectrum measurement. By tilting the crystal so that the X-rays do not pass through it along some important axis, different planes of the same form are inclined at different angles to the incident beam and consequently must reflect X-rays of different wave-lengths. By plotting the intensity of the reflection from planes belonging to the same form against the wave-lengths of the X-rays they are reflecting, points of a curve will be obtained which represents the effect of the X-rays upon the plate. The curves thus arising, one for each different kind of reflecting plane, can be compared in the same wave-length. The data so obtained [21] are serviceable in distinguishing be-

[21] S. Nishikawa: *Op. cit.* Ralph W. G. Wyckoff: *J. Am. Chem. Soc.*, **42**, 1100, 1920; *Phys. Rev.*, **16**, 149, 1920; *Am. J. Sci.*, **50**, 317, 1920.

tween the possible arrangements of atoms for the crystal under investigation.

Résumé.—A brief outline has now been given of the essential features of the three ways, as they exist at the present time, of attacking the problem of the structure of crystals. It may be well to collect the outstanding features of these methods to show how they are related to one another, and to indicate again the present status of the work in this field.

The start toward determining the arrangement of the atoms in crystals was made by looking around in each case for a structure which would explain the relative distances apart of planes of atoms in directions normal to a few crystal faces. Several chemically and crystallographically simple compounds—the alkali halides, zinc blende, the diamond, fluorspar—were thus studied. Assuming then that the structures thus obtained actually represent the arrangement of atoms within these crystals, the wave-length of X-rays was deduced with the aid of expression (1) from a knowledge of the density of the crystals and the number of molecules in the gram molecule. Further, taking this as the proper value for the wave-length of X-rays, we have proceeded to use it to determine the amount of mass to be associated with the unit of structure of every crystal which has subsequently been studied. The objection to this procedure is, as we have already pointed out, that those original structures, upon the correctness of which the value for the wave-length of X-rays has been based, have never themselves been shown to be the *only* structures which are in agreement with the experimental data. The strong indication of correctness given to this value of the wave-length by the fact that it fits in so satisfactorily with the large amount of data that has since accumulated makes this objection now a more or less formal one.

The determinations thus far made of the structure of crystals have been carried out by two distinct methods of procedure—or perhaps it would be better to say from two different points of view. Most of them have followed closely the early determinations in searching around for some grouping of atoms which would account for a certain limited amount of experimental data. The structures thus obtained have been considered to represent the actual arrangement of the atoms within the crystal. In many cases they are the simplest arrangements which could be found

and as such have a certain, but very doubtful, degree of probability. Without exception, probably, they are not, however, the only ones which could be fitted into the existing data.

Only a few crystals have as yet been studied, starting from the point of view suggested by the theory of space groups. Following such a method of procedure we would most ideally make use of all three ways of getting diffraction effects—the spectrometer, the method of powders and the transmission (Laue) photographs. The first step would get a reflection spectrum from some important crystal face. This measurement will decide the number of chemical molecules (or usually the numbers, since more than one is possible because of the uncertainty as to the order of the reflection) that can be associated with the unit underlying the crystal. With this as a basis, and using the results of the theory of space groups, *all* of the ways in which the atoms of the compound could possibly be arranged can be written down. It is then a comparatively simple matter to decide exactly what data are required to distinguish between these various possibilities and to get them by whichever of the three methods of obtaining diffraction effects will supply them most readily. Even if it is impossible, with the present limited amount of information about the mechanism of the reflection of X-rays, to eliminate all but one of these groupings, still we always have exact knowledge as to the status of the determination. The element of guessing is thus quite definitely eliminated.

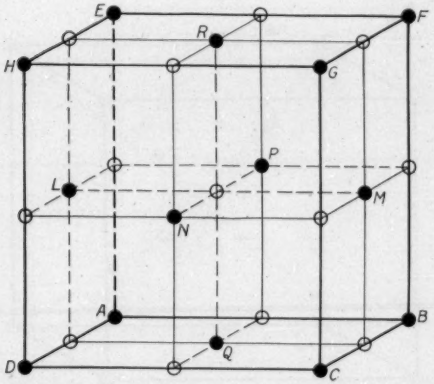
A DISCUSSION OF SOME OF THE STRUCTURES THUS FAR STUDIED.[23]

By making the seemingly plausible assumption that chemically simple compounds have their atoms in some sort of a simple arrangement in space, it is possible, as we have seen, to determine the crystal structures of quite a large number of compounds. It is perhaps worth while to consider to what results the structures obtained with the aid of this assumption will lead. A knowledge of the arrangement of the atoms in a crystal is essential to the adequate treatment of a large field of problems. The crystallographer who is concerned with finding some explanation for cleavage, or for a kind of twinning, will find an acquaintance with the crystal structure indispensable; the manner of the

[23] Not all of the crystals that have been studied will be discussed. Some, like fluorspar, CaF_2, cannot as yet be satisfactorily considered; many other determinations seem to be of more or less doubtful value.

arrangement of the atoms in a compound forms a rational basis upon which to build a discussion of the relative occurrences of crystal faces.[23] Furthermore the physicist who is interested in the structure of the atom must produce a model which will account for the structures of crystals. Yet again the chemist may look to these same structures for information as to the nature of the forces which are binding atoms together, for evidence of the existence or non-existence of the chemical molecule and for some light upon the nature of what we have been accustomed to call

FIG. 22.



The sodium chloride arrangement. The black circles represent the positions of the atoms of one kind; the white circles those of the second kind of atoms. The alkali halides and the oxides of the divalent metals seem to have this atomic arrangement. Either the black atoms or the white ones have the grouping of the closest cubic packing of spheres.

the valencies of the atom.[24] Quite recently attempts have been made to build upon these determinations of the structure of crystals a quantitative measure of such physical properties of the solid as its compressibility, as well as to try to explain, upon the basis of a definite model of the atom, some of the simpler struc-

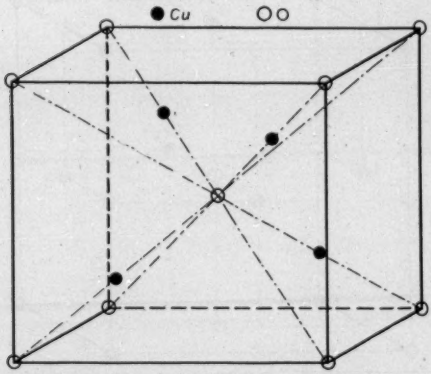
[23] Ralph W. G. Wyckoff: *Am. J. Sci.*, **50**, 317, 1920. P. Niggli discusses from this point of view the development of faces by crystals. *Zeit. anorg. Chem.*, 110, 55, 1920.

[24] For instance, see I. Langmuir: *J. Am. Chem. Soc.*, **38**, 2221, 1916; Ralph W. G. Wyckoff: *J. Wash. Acad. Sci.*, **9**, 565, 1919.

tures.[25] The problems of the chemist, while by no means necessarily the ones whose ultimate solution will be most easily obtained, are nevertheless the ones to which the sort of information furnished by a knowledge of the structure of crystals is most readily applicable. The data as yet at hand are so meagre—and the determinations themselves are, as already emphasized, of sufficient uncertainty—that the conclusions at which we arrive must be only provisional.

Metals.—The structures of a relatively large number of metals have been studied. Most of them appear to have the arrangements

FIG. 23.



The cuprous oxide arrangement. Each monovalent copper atom is surrounded by *two* equally distant oxygen atoms and each divalent oxygen atom by *four* copper atoms. The white atoms alone have the body-centred grouping.

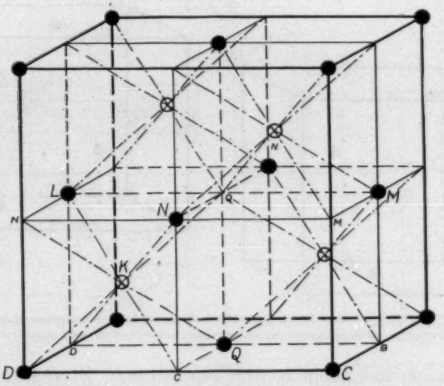
that would result from the close packing of bodies spherical or nearly spherical in shape. There are two forms of this close packing of spheres: (1) the closest packing, which has hexagonal symmetry, and (2) the more important cubic face-centred arrangement, which is nearly as close a grouping (Fig. 22). Aluminum,[26] silver, thorium, lead, copper, calcium, indium, pal-

[25] M. Born and A. Landé: *Verh. deut. Phys. Ges.*, **20**, 210, 1918; and several other papers by the same authors.

[26] A. W. Hull: *Phys. Rev.*, 10, 661, 1917; *Science*, 52, 227, 1920. P. Scherrer: *Phys. Z.*, 19, 23, 1918. H. Bohlin: *Ann. d. Phys.*, 61, 421, 1920. W. L. Bragg: *Phil. Mag.* (6), 28, 355, 1914. L. Vegard: *Phil. Mag.* (6), 31, 83, 1916.

ladium, and iridium are among the elements which have been shown to have this cubic close-packed grouping. Zinc,[27] cadmium, ruthenium, and magnesium, on the other hand, approach to the hexagonal closest packing. Several elements, however, such as iron,[28] chromium, titanium, sodium, tantalum, and tungsten crystallize in the less dense body-centred grouping (Fig. 23). Nickel [29] appears to be sometimes body-centred and sometimes face-centred. In attempting to deduce from these structures any information concerning either the bonding forces between the

FIG. 24.



The zinc sulphide arrangement. In this arrangement each white atom is distinct from four black atoms and each black atom from four white ones. If the black atoms are identical with the white ones, the arrangement is that which is found for the diamond.

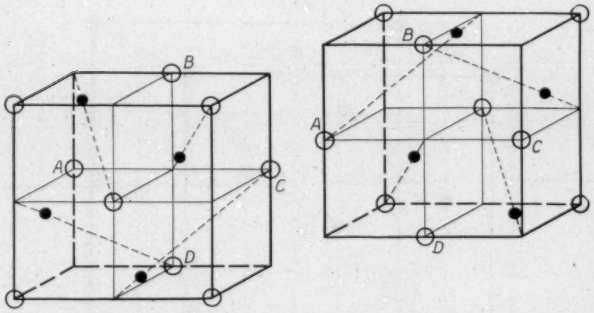
atoms or the structures of the atoms themselves, it must be borne in mind that there is always the possibility in a metal of one or more electrons functioning as "silent (so far as X-rays are concerned) partners" in the arrangement. For this reason the metals, though the simplest of compounds, are of all simple compounds perhaps the most dangerous as bases for further deductions.

Compounds of the Type AB.—Several compounds of the type

[27] A. W. Hull: *Op. cit.*
[28] A. W. Hull: *Op. cit.* P. Debye: *Phys. Z.*, **18**, 483, 1917.
[29] A. W. Hull: *Phys. Rev.*, 10, 661, 1917. H. Bohlin: *Op. cit.*

AB, where *A* is a metal atom and *B* is an electronegative atom, have been studied. All of the alkali halides have the "sodium chloride arrangement" (Fig. 22) wherein each atom has six atoms of the opposite kind equally near to it. The divalent metal oxides, magnesium and calcium, cadmium and nickel oxides,[30] all have this same structure. Galena (lead sulphide) exhibits the same grouping. Zinc blende (zinc sulphide), on the other hand, has a different structure (Fig. 24). In this case each zinc atom is surrounded by four equally distant sulphur atoms, while each

FIG. 25.



The pyrites arrangement. The black sulphur atoms are so spaced along the diagonals of these little cubes that each iron atom has six and each sulphur atom four equally near atoms.

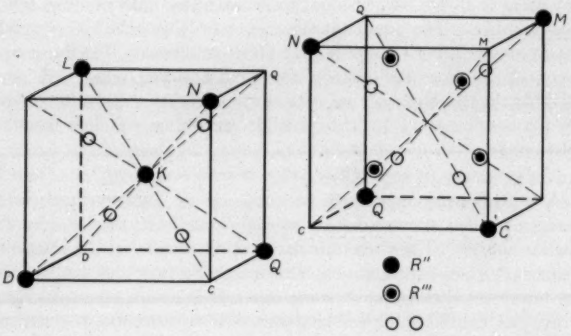
sulphur atom has about it four zinc atoms. Zinc oxide exhibits a still different grouping of atoms; but again each zinc atom is surrounded by four oxygen atoms while each oxygen atom has about it four zinc atoms. Cadmium sulphide and wurzite (hexagonal zinc sulphide) have the same atomic arrangement as zinc oxide.[31]

The immediate conclusion to be drawn from these structures is that there is no unique connection between the arrangement of the atoms composing them and their chemical valencies. A qualitative explanation of the structures of these compounds is nevertheless possible. From other evidence it has seemed probable that the atoms in crystals of potassium chloride and related compounds

[30] W. P. Davey and E. O. Hoffman: *Phys. Rev.*, **15**, 333, 1920.
[31] W. L. Bragg: *Phil. Mag.* (6), **39**, 647, 1920.

are electrically charged. Upon this basis, then, the alkali halides appear as aggregates of equal numbers of positively and negatively charged atoms. When the atoms are doubly charged, as is presumably the case with magnesium or calcium oxide, for instance, the distance between the atoms is much less than between those of the alkali halides. Calcium carbonate and the divalent carbonates isomorphous with it ($MnCO_3$, $FeCO_3$, etc.) have the same structures if the carbonate groups are substituted for the electronegative atom.[32] The large CO_3 group may be thought of as squeezing out the sides of the cube till it has the form of an

FIG. 26.



The spinel arrangement. The divalent metal atoms of a spinel occupy *all* of the positions of Fig. 24. The arrangement of the other atoms is here shown for the two typical divisions of this unit. Each divalent metal atom (R'') is equally distant from *four* atoms; each trivalent metal atom (R''') from *six* atoms; and each divalent oxygen atom (O) from *four* atoms.

obtuse rhombohedron. Similarly cæsium dichloroiodide ($CsICl_2$) has the same arrangement as cæsium chloride if the group of atoms ICl_2 is substituted for chlorine. In this instance the ICl_2 atoms are all strung along the body diagonal so that it may be imagined as distorted from a cube to an acute rhombohedron.[33]

Other Simple Compounds.—A number of other simple compounds have been studied with a considerable degree of care. If carbon atoms are placed at the positions occupied by both zinc and sulphur atoms in zinc blende, we obtain the

[32] W. L. Bragg: *Proc. Roy. Soc.*, A **89**, 468, 1914. W. H. Bragg: *Phil. Trans.*, A **215**, 253, 1915. Ralph W. G. Wyckoff: *Am. J. Sci.*, **50**, 317, 1920.

[33] Ralph W. G. Wyckoff: *J. Am. Chem. Soc.*, **42**, 1100, 1920.

arrangement of the atoms in the diamond (Fig. 24).[34] In pyrites each sulphur atom is surrounded by four equally distant atoms and each iron atom by six atoms[35] (Fig. 25). In cuprous oxide each copper atom is equally near to two oxygen atoms, while each oxygen atom has about it four copper atoms.[36] Magnetite, as a typical spinel, has been studied with great care, and in spite of its rather complicated chemical composition its structure is in all probability that given in Fig. 26.[37] In this case each divalent metal is surrounded by four, and each trivalent metal by six, equally distant atoms. In each of these cases it is to be noted that the number of the nearest atoms to any atom is always either equal to its chemical valence or is twice that number. The constant recurrence of this relation suggests that it may be other than purely an affair of chance. Furthermore, a consideration of the sorts of chemical bonding which are conceivable on the basis of our present knowledge of the structure of the atom points to the possible existence of just such a relation as this.

Information to be Derived from the Structure of the Atom.[38] —A neutral atom appears to be made up of a minute positively charged nucleus surrounded by enough electrons to neutralize the nuclear charge. The chemical inertness of certain of the elements —the rare gases of the atmosphere—and the fact that atoms having one, two, three, and in some cases four, more electrons than a rare gas, exhibit a marked tendency to lose just enough electrons in becoming positively charged to revert to the configuration of the inert gas, seem to point to the existence of certain especially stable configurations of electrons in atoms. For instance, sodium with one more and magnesium with two more electrons than neon readily lose one and two electrons respectively in becoming positive sodium and magnesium ions. Furthermore, as the electronegative elements are approached, a strong tendency becomes evident to add on enough electrons, beyond the number required for atomic

[34] W. L. Bragg: *Proc. Roy. Soc.*, A **89**, 277, 1913. W. H. and W. L. Bragg: *Ibid.*, 468.

[35] W. L. Bragg: *Op. cit.* P. P. Ewald u. W. Friedrich: *Ann. d. Phys.*, **44**, 1183 (1914).

[36] W. H. and W. L. Bragg: "X-rays and Crystal Structure," p. 155.

[37] S. Nishikawa: *Op. cit.* W. H. Bragg: *Phil. Mag.* (6), **30**, 305, 1915.

[38] J. J. Thomson: *Phil. Mag.* (6), **27**, 757, 1914. G. N. Lewis: *J. Am. Chem. Soc.*, **38**, 762, 1916. Ralph W. G. Wyckoff: *J. Wash. Acad. Sci.*, **9**, 565, 1919.

neutrality, to complete the next stable arrangement. If one of the atoms of a compound is highly electropositive and another strongly electronegative, the latter may be able to extract, as a result of this tendency, electrons from the positive atom; the compound in the solid state thus becomes, as we have supposed to be the case with the alkali halides, an aggregate of an equal number of positive and negative "ions." Such a union has been called a *polar bonding*. If, however, the combining atoms are both either strongly electronegative or are to be found among the elements of an amphoteric and less pronounced electrical character, then each atom will strive, without complete success, to abstract electrons from the other in order to complete its especially stable group. The electrons thus held in common by two atoms form a second sort of bonding—the *valency bonding*. Since a complete valence unit (in the old chemical sense) consists both of the tendency of one atom to acquire an electron from another and the tendency of some other atom to take one of this same atom's electrons, the number of electrons in combination with any particular atom may be twice as great as its chemical valence. Such valency bondings must be supposed to be operative between the atoms in those compounds of the sort discussed which are not of the sodium chloride type. This explanation accords well with the natures of such compounds as the diamond and carborundum, and accounts in a satisfactory manner for the unions between the chlorine atoms in chlorine gas or for the bonding between carbon and oxygen in the carbonate group. It is surprising, however, to find some metals, as zinc and copper (in zinc sulphide and cuprite), appear to exhibit the same sort of union in some of their compounds. It should be pointed out that the only metals for which this rule fits, iron, zinc, and the like, are without exception atoms in the centre of a long period of the periodic table. About the arrangement of the outside electrons of these atoms nothing is known at present. Of course it may be argued that we are dealing with only chance agreements with a rule, but it must be remembered that such structures as zinc sulphide depart so far from being closely packed arrangements of atoms that some sort of directional character to the forces of combination between their atoms seems necessary in order to account for their existence as stable groupings.

In spite of the obvious uncertainties that pervade all these dis-

cussions, there seems to be considerable evidence, from a consideration of the crystal structures of such compounds as have been more or less carefully studied, for the existence of two distinct types of solid compounds: (1) *polar compounds,* wherein the bonding between the atoms, or at least between certain groups of atoms, is polar; and (2) *valency compounds,* the atoms of which are bound to other atoms by holding electrons in common. A consideration of organic compounds, none of which have thus far been successfully studied using the X-rays, forces us to a third kind of compound; (3) the *molecule-forming compounds,* built of groups of atoms (the chemical molecules) held together presumably by relatively weak stray fields of force. It will be noticed that in solids of the first two types no molecules in the chemical sense of the word exist: each crystal or piece is a single chemical individual.

DECEMBER, 1920.

A Qualitative Reaction for Magnesium.—F. EISENLOHR (*Ber.,* 1920, vol. liii, 1476) describes the following test for magnesium. An alcoholic solution of alkanet root is prepared and to 5 c.c. of it is added a drop of ammonium carbonate solution of 2N strength. This produces no appreciable change of color, but if additions are made of a few drops of neutral solutions of either magnesium, barium, calcium, strontium or manganous salts the following effects are respectively produced:

Magnesium	Barium	Calcium	Strontium	Manganese (ous)
blue violet	no change	blue	blue violet	blue violet

The colorations produced by magnesium, strontium, and manganous salts are not strikingly different, but if the solution is acidified with not more than two drops of 2N hydrochloric acid, the liquid changes to bright red, and then, if again rendered alkaline by a like volume of ammonium carbonate solution, becomes, in the presence of magnesium, blue violet. In dealing with an ordinary phosphate precipitate, this is dissolved in 2N hydrochloric acid, and a portion of the alkanet solution is mixed with a drop of the acid solution, and then one to two drops of the ammonium carbonate solution, when the presence of a magnesium compound will be shown by the production of the blue violet. If magnesium is not present, the original color of the alkanet solution will appear.

The alkanet solution must not be diluted with water, as this will give rise to a hydrolysis of the ammonium carbonate by which ammonium hydroxide will be produced.

H. L.

FLASHING SPEEDS OF INCANDESCENT SIGNAL LAMPS.*

BY

A. G. WORTHING.

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SYNOPSIS.

THIS paper represents a portion of a study of the theory of signalling units involving incandescent lamps, which was undertaken in response to a request from the National Research Council and the U. S. Signal Corps for the development of a unit for use in daylight signalling.

Filament Characteristics Involved.—Various factors involving signalling speed, where the telegraphic dot-and-dash signals are produced by the flashing of an incandescent lamp, are discussed broadly in a contrast of tungsten with carbon for filament material. The most important factors are: (1) the change in resistance with change in temperature; (2) the quantity of energy required to heat the filament through a given temperature range; (3) the total emissive power of the filament material; (4) the maximum temperature of a flash, and (5) the efficiency of the radiation in producing vision. For lamps of equal voltage, life and luminous flux, a tungsten filament responds more rapidly than carbon during the heating portion of a flash by a factor of six or seven; during the cooling portion of a flash by a factor of 2.5.

Observed Speeds and Their Comparison with Computed Values.—A photometric method of studying the performance of lamps on flashing is described and results obtained with various lamps are presented. These are compared with computed values based on steady current measurements and the supposition that a lamp filament on heating or cooling passes through a succession of steady states. The agreement is quite satisfactory, excepting the case of a filament immersed in hydrogen, where the discrepancy may be ascribed to ionization effects.

Speed Function.—A simple function Q (equation 12), involving only steady current measurements of wattage, resistance

* Communicated by the Author.

and temperature in the neighborhood of the maximum temperature of a flash, together with a knowledge of the thermal capacity of the filament, will serve quite accurately in rating lamps as to their flashing speeds.

Some Fundamental Generalizations.—(1) The time required for a filament to heat to approximately its maximum brightness exceeds greatly the time required in cooling to effectively zero brightness.

(2) The higher the maximum temperature of a flash, the greater is the speed of the flash.

(3) The smaller the filament, the greater is the speed of the flash.

(4) The less the resistance in a circuit external to a flashing tungsten lamp, the greater is the speed of the flash.

(5) The speed of flashing for a given filament at a given temperature in various atmospheres—including in vacuo—is greater, the greater the gas loss.

(6) For lamps of the same open filament construction, the same luminous flux, and the same average life at a fixed voltage, the speed of flashing is greater, the greater the gas loss.

Ribbon Filaments Versus Wire Filaments.—The quantity of material in a ribbon filament is less than that in an equivalent wire filament. Therefore, in gas-filled lamps, by going from a wire filament to a ribbon filament we may obtain either a considerable increase in signalling speed, or, often without a reduction in speed, a higher efficiency by choosing an atmosphere involving a decreased gas loss. For example, a lamp containing a ribbon filament in argon, proposed in response to the above request, when compared with a lamp containing a wire filament in nitrogen which was its nearest competitor, indicated speeds and efficiencies in favor of the ribbon filament lamp of about 1.6 and 1.25.

IMPORTANCE OF VARIOUS FACTORS AS INDICATED IN A CONTRAST OF TUNGSTEN AND CARBON FILAMENT LAMPS.

It is a matter of common observation that an ordinary tungsten lamp lights up more quickly than does an equivalent carbon-filament lamp. The contrast, most evident when the older types of carbon lamps are considered, is still quite appreciable for the

later Gem lamps containing the metallized graphite filament. This difference in response between tungsten and carbon filaments may be readily analyzed to show the various factors which determine the flashing speeds of signal lamps.

The fundamental law descriptive of the behavior of all incandescent lamps which is applicable here, states that the rate of supply of energy as heat to a filament is equal to the rate of dissipation of energy by the filament plus the rate of storage of energy in the filament. The dissipation of energy may take place through radiation, through ordinary heat conduction to filament supports or through gaseous conduction and convection. In vacuum lamps, of course, no gas losses are present. This law is expressed in equation form as

$$VI = f(T) + cm\frac{dT}{dt} \tag{1}$$

where V represents potential drop, I current, $f(T)$ rate of dissipation of energy at a temperature T, c specific heat, m filament mass, and $\frac{dT}{dt}$ rate of increase or decrease of temperature. The three terms of the equation correspond respectively to the three rates enumerated in the underlying fundamental law. For brevity of reference these will often be referred to as supply rate, dissipation rate and storage rate. During the first part of a flash the storing up of energy in the filament is by far the predominating method by which the supply is disposed of. With increasing temperature the dissipation method becomes more and more effective until, at the maximum temperature, the dissipation rate equals the supply rate and the storage process ceases.

Evidently those factors which affect the flashing speeds of signal lamps do so through affecting the supply rate, the dissipation rate, the amount of energy to be stored up, and, since flashes are measured from a brightness instead of a temperature standpoint, the percentage change in brightness accompanying a given percentage change in temperature.

In contrasting the flashing properties of different filaments, there appear certain factors more or less independent: (1) the change in filament resistance with change in temperature; (2) the quantity of energy required to heat the filament through a given temperature range; (3) the total emissive power of the filament material; (4) the maximum temperature of the flash, and (5) the

efficiency of the radiation from the filament in producing vision. It is interesting and worth while to consider how and to what extent these factors are of importance individually. With this in mind, let us contrast the heating up portions of the flashes (omitting for the present that portion of the flash during which cooling occurs) of equivalent vacuum tungsten and Gem lamps in circuits, encountered in signalling practice, containing constant voltage sources with no appreciable resistance external to the lamp.

Factor (1) relating to changes in filament resistance with changes in temperature concerns the supply rate. In tungsten an exceptionally large increase in resistance—of the order of thirteenfold—occurs in heating from room temperatures to ordinary incandescent temperatures; in the Gem lamp the resistance change is practically nil. In the constant voltage circuit met with in signalling practice, a tungsten filament, in consequence of its low initial resistance, experiences a proportionally large initial current, and a correspondingly large initial supply rate. The initial storage rate is equally great. With the gradual increase in temperature and resistance, a gradual diminution occurs in the supply rate until the maximum temperature is reached. The supply rate for the Gem filament in a like circuit is practically constant. Comparing now tungsten and Gem lamps of the same voltage and the same wattage, in which therefore the final supply rates are equal, cause is seen for a great advantage in flashing speed through the use of tungsten. Computations according to a method detailed later, indicate that a tungsten filament operated in a circuit with a constant supply rate reaches 90 per cent. of its maximum brightness in an interval about 1.6 times that required when operated in the constant voltage circuit of normal signalling. Most of the actual difference in time is represented by a delay in heating through the lower range of temperature. The advantage of a tungsten filament over a Gem filament in the heating portion of a flash resulting from changes in resistance may thus be set down as about 1.6.

Factor (2), relating to the thermal capacity of the lamp filament, concerns the storage of heat in the filament. Various measurements on Gem and tungsten lamp show, for the same voltage, wattage and operating temperature, that the heat stored up in the Gem filament is about 1.3 times that stored up in the tungsten filament. The advantage of a tungsten filament over a

Gem filament resulting from differences in the thermal capacity of the filaments is thus of the order of 1.3.

Factor (3) relating to total emissive powers concerns the dissipation rate. The total emissive power of tungsten—the measure of its rate of radiating energy compared with a black body at the same temperature—is generally low, though increasing rather rapidly with increasing temperatures. The total emissive power of a Gem filament is comparatively high and does not change rapidly with changing temperatures. The radiation rates for the lamps being compared represent practically the dissipation rates as defined, and, at their maximum temperatures, are therefore approximately equal to their supply rates. But, on the passage of the filaments through the lower temperature ranges, due to the relatively smaller emissive power (expressed in terms of the value at the maximum temperature) of tungsten, there is relatively a reduced rate of radiation of energy by that metal and thereby a comparatively increased storage rate. Though the advantage is definitely in favor of tungsten, the effectiveness of this factor is small, and for our comparison, may be considered negligible.

Factor (4), relating to the maximum temperature of operation, concerns the supply rate, the dissipation rate and the quantity of heat stored up. Comparing two tungsten lamps of the same voltage and wattage, but with operating temperatures of 2200° K,[1] approximately that of the Gem lamp, and 2400° K approximately that of the low wattage vacuum tungsten lamp, we find that the change in the dimension of the filament in going from the lamp with the lower operating temperature to that with the higher operating temperature is considerable, and that the increase in the quantity of heat stored up resulting from the increased temperature range is much more than offset by the less amount of material heated. The net advantage resulting from the higher temperature is about 1.6. The effect on the supply rate results from the increased change in resistance, an effect already accounted for. The effect on the dissipation rate concerns changes in total emissive power, an effect also already accounted for. The advantage of a tungsten filament over a Gem filament in the heat-

[1] Temperatures in the thermodynamic centigrade scale are commonly measured in degrees K. (Kelvin), the zero of which scale is the absolute zero of temperature. °K. = °C. + 273°.

ing portion of a flash, resulting from the higher operating temperature of the former, is thus about 1.6.

Factor (5), relating to the luminous efficiency of radiation, is the most important factor in the contrast of speeds. It concerns the supply rate and the amount of heat that is stored up. In the preceding paragraphs, equality of voltage and of wattage has been the basis on which lamps have been rated as equivalent. A more just basis, since the eye is the instrument by which flashing signals are tested, is one of equality of voltage and of luminous output. It is in this transition that luminous efficiency considerations enter. Contrasting an efficiency of 4.1 lumens per watt for the Gem lamp with 9.2 lumens per watt for the tungsten lamp at 2400° K, shows that for equivalent lamps from the visual standpoint, the wattage of the tungsten lamp should be only about 45 per cent. of the wattage of the Gem lamp. Considering now two lamps of the same filament material, differing in wattage in this same ratio, it follows that the smaller filament is only 77 per cent. as long, 59 per cent. as great in diameter and 27 per cent. as great in mass as the larger filament. The combined effect of the decreased filament mass and decreased supply rate leads to a flashing speed in favor of the smaller filament equal to about 1.7. Evidently this reasoning may be applied to the case where filament materials are contrasted. The advantage of a tungsten filament over a Gem filament in the heating portion of a flash resulting from differences in the luminous efficiencies of their radiations is thus of the order of 1.7.

Combining the several advantages possessed by tungsten, one would expect that a tungsten lamp flashed in a constant voltage circuit to its normal operating temperature, would reach 90 per cent. of its maximum brightness in somewhat more than one-sixth of the time required by an equivalent Gem lamp flashed to its normal operating temperature. At the time this comparison was conceived the apparatus described later had been dismantled, so that no direct experimental verification of the preceding considerations is offered. However, computations according to the method indicated later point to the real contrast in speeds of the two lamps as being about 1:6.5. This is a very satisfactory agreement indicating the correctness of the analysis.

The cooling portion of a flash might be analyzed similarly. However, such a comparison is relatively of much less importance

in contrasting filaments for flashing speeds, because the time required for a filament to cool to a negligible fraction, say 5 per cent., of its maximum brightness, is always small in comparison with the time required to heat to 95 per cent. of the maximum brightness. Briefly stated, such an analysis summarized shows that a tungsten lamp during the cooling portion of a flash will respond about 2.5 times as rapidly as the equivalent Gem lamp. The superiority of a tungsten over a Gem filament in incandescent signal lamps is decisive.

In this work, started in response to a request for the development of a unit for use in daylight signalling, emphasis is laid upon variations in tungsten-filament lamps, since simple considerations like those stated above showed them to be much more desirable than any known lamps containing filaments of different material.

EXPERIMENTAL METHOD.

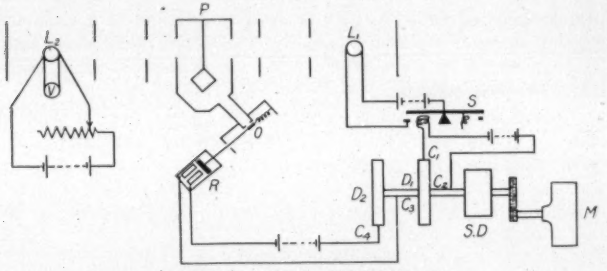
The experimental study of flashing speeds was based upon a method used previously.[2] It consisted in making instantaneous candlepower measurements of a flashing lamp at various instants following the beginning or ending of a current flash.

The arrangement of apparatus used is diagrammed in Fig. 1. L_1 represents the lamp being flashed, L_2 a comparison lamp operated under steady current conditions, P an ordinary photometer head for instantaneous candlepower comparisons of L_1 with L_2. The flashing of L_1 was brought about by the periodic making and breaking of the current through it by means of the electromagnetically operated switch S. Regularity of action and the precise value of the period depended upon the synchronous motor which operated two sliding contacts C_1 and C_2 in the same circuit with the electromagnet of the switch. Positiveness in the action of the switch was secured by means of a spring as shown, which tended to keep it open. Ordinarily the adjustments were such that the circuit containing L_1 was closed only during a quarter turn of the drum D_1. Drum D_2 mounted on the same shaft as D_1 carried an adjustable point contact C_4, which closed once each rotation of the drum, the circuit containing the relay R for a very brief interval only. The operation of R in turn jerked aside momentarily a small opaque screen at the opening of the photometer eyepiece O. For any particular setting of the point

[2] *Lighting Journal*, Nov. 1915; *Phys. Rev.*, 12 p. 199, 1918.

contact on D_2, there was a definite phase relation between the exposure of the opening at O and the flash of the lamp L_1. This condition permitted the observer, in arriving at candlepower com-

FIG. 1.

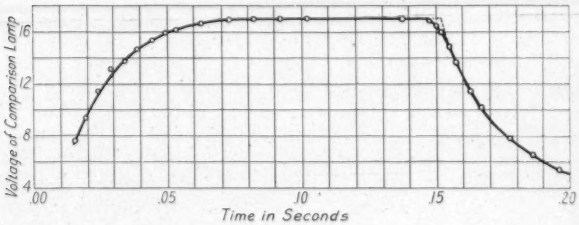


Apparatus for testing speed of signal lamps.

parisons between L_1 and L_2, to use any desired number of successive glimpses of the photometric field.

The method of procedure consisted in judging for some definite setting of the contact C_4, the momentary deviations from equality in the photometric match, adjusting the current through

FIG. 2.

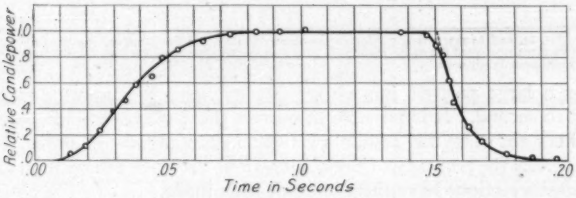


The voltage of a comparison lamp required to match in candlepower a 6-volt, 2-ampere, argon-filled, ribbon-filament signal lamp on flashing, as a function of time.

lamp L_2 for equality, and noting the voltage of lamp L_2. Then the operator adjusted the contact C_4 to a new position and proceeded as before. From a number of such readings, a curve may be platted, showing the voltage of the comparison lamp L_2 as a function of the time elapsing since the beginning of the flash in the

lamp L_1. Such data for a special argon-filled, ribbon-filament lamp [3] are platted in Fig. 2. The consistency of the observations is well shown. Given further the relation between voltage and candlepower for lamp L_2 there follows at once, as shown in Fig. 3, the candlepower variations of the special lamp during a flash. In this case the lamp practically reached its maximum steady candlepower in somewhat less than a tenth of a second. On cooling off the luminous output fell to a few per cent. of its maximum value in considerably less than a twentieth of a second. The consistency obtainable in measurements of this character is shown in Table I, in which certain speed characteristics are given for various lamps proposed for signal purposes.

FIG. 3.



The candlepower as a function of time for a 6-volt, 2-ampere, argon-filled, ribbon-filament signal lamp, on flashing.

It is evident that the observed curves, in case strictly instantaneous glimpses could have been obtained, would have followed much the paths indicated by the dotted lines in Figs. 2 and 3; but, due to the aperture at O being open for an appreciable interval, the cooling effect became manifest previous to the coincidence in time of the interruption of the flashing current and the centre of the time interval during which the opening at O was uncovered. This is quite analogous to the effects due to finite slit-widths in spectrophotometry. The difference in time given by the intercepts of the full and dotted curves on the steady maximum candlepower line represents one-half of the interval of exposure of the photometric field. The total exposure in this instance, as well as

[3] This lamp was a preliminary lamp of the type recommended by the Nela Research Laboratory for use in a 6-volt, 2-amp. signalling unit for the U. S. Signal Corps. The possibility of manufacturing ribbon filament lamps has depended upon the production of satisfactory ribbon filaments, an accomplishment brought about by Dr. C. F. Lorenz, formerly of this laboratory.

TABLE I.

Data on Ribbon and Wire Filament Signal Lamps Showing Consistency in Speed Measurements.

Lamp	Description	V in Volts	I in Amperes	r/R_m	T	Heating *		Cooling*
						$t_{.2}-t_0$	$t_{.7}-t_{.2}$	$t_{.2}-t_{.7}$
26L	Very open double spiral 0.025 mm. ribbon filament in argon at 600 mm. pressure	7.05	2.15	0.12	3020°K	.....	0.019 sec.	0.016 sec.
							.020	.013
							.015	.019
							.019	
							.019	
							.017	
							.020	
80S	Very open double spiral 0.083 mm. wire filament in nitrogen at 600 mm. pressure	5.80	1.91	.04	2980	0.036 sec.	.030	.014
						.037	.028	.015
						.036	.026	
						.039	.027	
							.031	
							.031	
S-133-Ar	Moderately open single spiral 0.027 mm. ribbon filament in argon at 600 mm. pressure	6.60	1.84	.16	3020	.....	.029	.017
							.026	
							.030	
							.028	
							.030	

* t_0, $t_{.2}$, and $t_{.7}$ respectively refer to the time at which the flash began, the time at which the filament possessed 0.2 of its maximum brightness, and the time at which it possessed 0.7 of its maximum brightness.

for a large part of the work reported here, was approximately 0.010 second. It is possible to correct these curves and to obtain others showing the results of truly instantaneous glimpses, but generally the accuracy of the observations does not justify this, and such corrections have therefore not been made.

EXPECTATIONS BASED ON STEADY CURRENT MEASUREMENTS.

Before discussing the experimental data, let us consider the flashing speeds which steady current measurements lead us to expect. We shall assume that there is no lag or lead of radiation with respect to resistance [4] during the rapid changes of temperature incident to the flashing of a filament. For a circuit containing no resistance external to the flashing lamp, equation (1) reduces to

$$\frac{V^2}{R} = W + cm\,\frac{dT}{dt}, \tag{2}$$

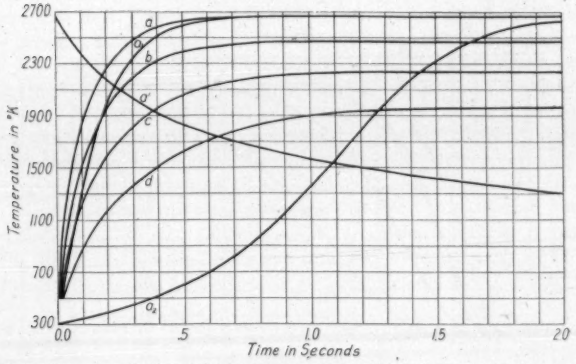
in which V represents the steady voltage of the battery; R the resistance of the lamp; W the steady wattage corresponding to R; and the other symbols the quantities as already mentioned. Solving for $\frac{dt}{dT}$, we have

$$\frac{dt}{dT} = \frac{cm}{\frac{V^2}{R} - W}. \tag{3}$$

[4] Worthing, *Phys. Rev.*, **12**, p. 199, 1918: Gæhr. *Phys. Rev.*, **12**, p. 396, 1918.

This equation, together with data showing the relation between resistance, wattage and temperature for a succession of steady states, serve for the computing of the time dt required, for any small change in temperature, dT. The summation of such small intervals of time over any arbitrarily chosen temperature range gives directly the time required to heat the filament through that temperature range. Similar summations for a number of arbitrarily chosen temperature ranges serve for the platting of a curve

FIG. 4.



Heating and cooling curves for a 0.258 mm. tungsten filament in vacuo-lamp A-33.

Curve	Condition	r/R_m	T_m
a	Heating	0	2667°K.
b	Heating	0	2478°K.
c	Heating	0	2232°K.
d	Heating	0	1973°K.
a_1	Heating	.17	2667°K.
a_2	Heating	∞	2667°K.
a'	Cooling	—	2667°K.

showing the temperature of a flashing filament as a function of time.

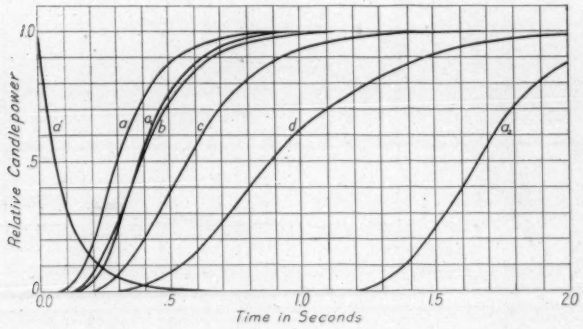
Making use of the relations between R, W, T, and c, found for a certain tungsten vacuum lamp,[5] $A-33$, flashing curves were computed for various conditions of operation. Fig. 4, curves a, b, c, and d, represent four such curves computed for this lamp in constant voltage circuits containing no resistance other than that of the lamp filament. The curves show that the

[5] *Loc. cit.*

flashing speed for a given filament diameter increases rapidly with increase in the maximum temperature.

The term $\frac{V^2}{R}$ of equation (2) is ordinarily zero during the cooling process, and the changes which take place depend only on the state of the filament itself. It follows that whatever the maximum temperature of the flash, the cooling curves for a given filament through a specified temperature range are identical. For example, a filament heated to 2500° K, after cooling to 2000° K, will thereafter cool exactly as though heated initially only to 2000° K.

FIG. 5.



Candlepower time curves corresponding to the temperature time curves of Fig. 4.

When the circuit contains resistance external to the flashing lamp equation (3) reduces to:

$$\left(\frac{V}{R+r}\right)^2 R = W + cm\,\frac{dT}{di} \tag{4}$$

where r represents the external resistance. A contrast of curves a and a_1, Fig. 4, shows the effect of the introduction of a moderate resistance; a contrast of curves a and a_2 the effect of an extremely large resistance. In this instance, the ordinarily favorable effect of the positive-temperature coefficient of the tungsten filament has become an equally great detriment to rapid flashing.

Fig. 5 shows the brightness curves corresponding to the temperature curves given in Fig. 4. The desirability of a high operating temperature and a circuit free from external resistance

for rapidity of flashing are perfectly evident. The most evident effect of an external resistance, as has been stated already, is a delay in the appearance of incandescence. It is also to be noted that the time required in cooling down from the maximum brightness to say 5 per cent. of that value is considerably less than that required to heat from room temperature to within the same per cent. of the maximum value, that is to 95 per cent. of the maximum value. This agrees with what has been said already regarding the predominating importance of the heating portion of a flash in determining flashing speeds. This conclusion may seem at variance with common observations on effects noticeable on switching on and off ordinary lamps. The apparent discrepancy is to be ascribed largely to the inertia of the pupillary aperture of the eye and to changes in the retina sensitiveness to light stimuli. On the flashing up of a lamp both factors operate to give the impression of a maximum brightness, or of an overshooting in brightness while the filament is still relatively far from the actual maximum brightness.

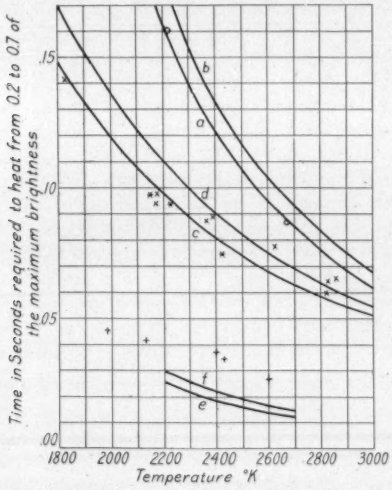
Corresponding curves for filaments of the same material, but of different radii, may be obtained from the curves of Fig. 4 and Fig. 5. It may be readily shown, referring to equation (3), that $\frac{V^2}{R}$ and W for a given length of wire both vary as the radius of the filament, while the mass varies as the square of this dimension. This results in corresponding values for $\frac{dt}{dT}$ varying directly as the radii. Therefore, for a filament whose diameter is 0.0258 mm., one-tenth that of the filament considered in Figs. 4 and 5, corresponding curves may be obtained at once from the curves of those figures by dividing the time intervals by ten.

Curves *a* and *b*, Fig. 6, show the computed results for a vacuum lamp having a filament whose diameter is 0.0134 mm. for the condition of no resistance external to the lamp and for a condition of a resistance equal to about one-sixth that of the filament when at 2667° K, the approximate conditions occurring in experimental work with this same size of filament.

The flashing speed for a filament immersed in a gas may be computed on the supposition that the lamp filament on heating up passes through a succession of steady states; that is, on assuming that a filament on passing through 1500° K on its way to a

maximum temperature of 2500° K is radiating and losing energy by gaseous conduction and convection at the same rate as it radiates and loses energy in consequence of the gas when operated at a steady temperature of 1500° K. Equations (3) and (4)

FIG. 6.



Times required for lamps with 0.134 mm. tungsten wire filaments to heat from 0.2 to 0.7 of their maximum brightnesses under various conditions, usually corresponding roughly to computed curves *b*, *d* and *f*.

Symbol	Lamp (See Table II)
o	S–150–*V*
x	S–150–*Ar*
*	S–142–*Ar*
+	S–158–*H*

Curve	Atmosphere	$r/R_{2667°K.}$
a	Vacuum	0.00
b	Vacuum	0.17
c	Argon at 600 mm.	0.00
d	Argon at 600 mm.	0.17
e	Hydrogen at 600 mm.	0.00
f	Hydrogen at 600 mm.	0.17

then become applicable to gas-filled lamps as well as to vacuum lamps. It should be noted here that the quantity W includes the gas loss. Following this plan, curves *c* and *d* of Fig. 6 have been computed for a 0.0134-mm. tungsten filament in argon, and curves *e* and *f* for the same lamp when hydrogen filled. Due to

changes in the relative importance of gas conduction with change in filament size, one cannot compute the speeds for one size of filament in terms of those for another size by the simple method shown for vacuum lamps.

EXPERIMENTAL RESULTS.

For comparisons of signalling speeds it is necessary to adopt some criterion of flashing speed. Since all candlepower-time curves seem to have the same shape and to differ mainly in their relative slopes, a measure of their relative slopes would seem a fair criterion. This criterion is not all that could be wished since it does not take account of the time interval required for the filament to reach incandescence. As a measure of this slope and criterion, we have arbitrarily adopted the time required for a filament in heating from two-tenths to seven-tenths of its maximum brightness. This represents referring to Fig. 3, the time of passage through what is sensibly the straight portion of the heating curve. Thereby, also, the errors due to the finite lengths of the glimpses of the photometric field in the experimental work were largely eliminated.

Observed values for such speed criterions are contrasted in Table II and Fig. 6 with the computed values for various lamps. While the agreements are not all that could be desired, they are not bad considering experimental difficulties.

Certain causes for these outstanding differences may be briefly stated. (1) Due to the finite length of glimpses in the photometric measurements, observed values for $t_7 - t_2$ may be expected to be too great, the more so the smaller the value of $t_7 - t_2$. Consideration of apparent lengths of glimpses indicates negligible effects for $S-142-Ar$, $S-150-Ar$ and $S-150-V$; but in the case of $S-140-Ar$ and $S-158-H$ these effects may amount to 10 per cent. or more. (2) The end coolings of the filaments in $S-150-Ar$, $S-150-V$ and $S-158-H$ were different from those in the lamps used in computation. Their influence becomes more and more prominent with decreasing temperature of flash. Just how this would affect the results is difficult to say. (3) Hydrogen molecules, as shown by Langmuir,[6] dissociate at high temperatures. Above 2000° K or 2100° K, the fractional part

[6] *Trans. Am. Electrochem. Soc.*, 20, p. 225. 1911; *Phys. Rev.*, 34, p. 401, 1912; *Jour. Am. Chem. Soc.*, 34, p. 860, 1912.

of the molecules in a given mass that are thus split becomes quite appreciable. Flashing lamps containing hydrogen, therefore, possess an added method of disposing of energy supplied, which does not occur appreciably in other lamps. A hydrogen lamp as its filament heats up is required to establish and maintain a more and more completely ionized atmosphere. There is in effect

TABLE II.

Observed and Computed Values of the Rates of Heating and Cooling of Various Tungsten Filaments.

Lamp	Description	$R\frac{r}{m}$	Maximum temperature of flash	Heating *				Cooling *	
				$t_{.2}-t_0$		$t_{.7}-t_{.2}$		$t_{.2}-t_{.7}$	
				Obs. Sec.	Comp. Sec.	Obs. Sec.	Comp. Sec.	Obs. Sec.	Comp. Sec.
S–140–Ar	Straight 0.039 mm. filament in argon at 600 mm.	0.010	2780°K.	0.021	0.014	0.022	0.013	0.009	0.0056
		.011	2490	.026	.018	.022	.016	.007	.0058
		.013	2220	.028	.022	.024	.019	.010	.0058
		.009	2720	.024	.015	.023	.014		
S–142–Ar	Straight 0.134 mm. filament in argon at 600 mm.	.08	2825	.072	.080	.060	.062	.027	.030
		.12	2220	.130	.158	.095	.102	.039	.036
		.28	1855	.216	.....	.103(?)	.162	.036	.039
		.22	2420	.104	.132	.075	.090	.028	.034
		.15	2165	.153	.166	.098	.110	.043	.037
S–150–Ar	Openly coiled 0.134 mm. filament in argon at 600 mm.	.16	1980	.183	.193	.110(?)	.134	.035	.038
		.14	2845	.091	.077	.066	.062		
		.18	2615	.101	.106	.077	.075		
		.19	2380	.133	.137	.088	.090		
		.17	2190	.158	.163	.094	.109		
		.21	2395	.127	.149	.085	.091		
		.24	1860	.234	.247	.141	.159		
		.14	2825	.087	.080	.065	.063		
S–150–V	Openly coiled 0.134 mm. filament in vacuo.	(?)	2190	.150	(?)	.098	.109		
		.14	2680	.097	.091†	.086	.095		
		.17	2220	.141	.154†	.160	.174	.053	.060
S–158–H	Openly coiled 0.134 mm. filament in hydrogen at 600 mm.	.18	2125	.068	.041	.041	.....	.013	.008
		.17	2420	.050	.034	.021	.....	.013	.008
		.14	2600	.035	.028	.017	.....	.012	.007
		.16	2405	.047	.039	.022			
		.20	1975	.059	.042				

* t_0, $t_{.2}$ and $t_{.7}$ respectively refer to the time at which the flash began, the time at which the filament possessed 0.2 of its maximum brightness, and the time at which it possessed 0.7 of its maximum brightness.

† Account has been taken here of the fact that in the vacuum lamp the filament did not cool to sensibly room temperature between flashes.

an added appreciable method of storage of energy for the filament not considered in equations (2) and (3). This factor is extremely difficult to allow for, but, when taken into consideration, must lead to greater computed values for $t_7 - t_2$, thus lessening the outstanding difference between the observed and the computed values. A contrast of results on $S-140-Ar$ and $S-158-H$ lends credence to this view. (4) The supposition that filaments in gas-filled lamps pass through a succession of steady states is not completely fulfilled. This unquestionably accounted for several

cases of burn-outs on first flash in some low-voltage signal lamps which were operated at exceptionally high temperatures, though the same lamps had previously withstood for some time the same high temperatures when brought to them gradually.

Summarizing the tests on the flashing speeds, it appears that computed values for the times required to reach two-tenths of the maximum brightness ($t_{.2} - t_0$) and to go from this condition to seven-tenths of the maximum brightness ($t_{.7} - t_{.2}$) on heating, and then to cool through this same range ($t_{.2} - t_{.7}$) agree well with the observed values in the vacuum and argon-filled lamps containing 0.134-mm. filaments. Considering sources of error, the differences in $S - 140 - Ar$ and $S - 158 - H$ may well be accounted for. If we except hydrogen-filled lamps in which ionization occurs, we probably are not far wrong in assuming that the true values of the speed criterions may be obtained by computation, using the method outlined above. In general we may say in comparing various types of tungsten filament lamps, that the time required for a filament to heat to approximately maximum brightness exceeds greatly the time required in cooling to approximately zero brightness; that the higher the maximum temperature of a flash the greater the flashing speed; that the smaller the filament the greater the flashing speed; that a given filament in hydrogen flashes more rapidly than in argon, and more rapidly in argon than in vacuo.

SPEED FUNCTION FOR RATING LAMPS.

It has already been noted in connection with Fig. 5, that the general form of the candlepower-time curve for a tungsten filament in vacuo, in a constant voltage circuit is not much changed by changing the maximum temperature of the flash or by introducing a small external resistance in the circuit. It might be added that changes in filament size and immersion in gas are likewise of little effect in changing the general aspects. This leads one to suspect that some function might be found which would represent the facts well enough to be taken as a cue to the speed of the lamp. With this in mind consider the rate of change of brightness of a filament with time at or near the maximum temperature during the heating portion of a flash. Equation (4) on rearranging gives

$$(5) \qquad \frac{dT}{dt} = \frac{W_m}{cm}\left[\frac{R/R_m}{\left(\frac{R+r}{R_m+r}\right)^2} - \frac{W}{W_m}\right]$$

Making use of the oft-used expressions

$$\frac{R}{R_m} = \left(\frac{T}{T_m}\right)^{\alpha} \tag{6}$$

and

$$\frac{W}{W_m} = \left[\frac{T}{T_m}\right]^{\beta} \tag{7}$$

where α and β are constant for temperatures not far removed from the maximum temperature, T_m, and expanding, we have

$$\frac{R}{R_m} = \left(1 - \frac{T_m - T}{T_m}\right)^{\alpha} = 1 - \alpha\,\frac{T_m - T}{T_m} + \alpha\,\frac{(\alpha - 1)}{2}\left(\frac{T_m - T}{T_m}\right)^2 - \ldots . \tag{8}$$

and

$$\frac{W}{W_m} = \left(1 - \frac{T_m - T}{T_m}\right)^{\beta} = 1 - \beta\,\frac{T_m - T}{T_m} + \frac{\beta(\beta - 1)}{2}\left(\frac{T_m - T}{T_m}\right)^2 - \ldots . \tag{9}$$

similarly

$$\left(\frac{R + r}{R_m + r}\right)^2 = \left[1 - \frac{R_m}{R_m + r}\left(1 - \frac{R}{R_m}\right)\right]^2 = \left[1 - \frac{R_m}{R_m + r}\,\alpha\,\frac{T_m - T}{T_m}\left(1 - \frac{\alpha - 1}{2}\,\frac{T_m T}{T_m} + \ldots .\right)\right]^2 \tag{10}$$

For temperatures near the maximum, the first two terms of each expansion may be used with but slight errors to replace the infinite series to which they belong. We have then on substituting in (5) for temperatures near T_m

$$\frac{dT}{dt} = Q\,(T_m - T) \tag{11}$$

where

$$Q = \frac{W_m\left(\beta + \alpha\,\dfrac{R_m - r}{R_m + r}\right)}{(CM)_m T_m} \tag{12}$$

Insofar as (11) is exact, Q is a time constant for the flash, indicating that the rate of increase temperature of a flashing filament in a constant voltage circuit is proportional to the temperature difference $(T_m - T)$. A similar expression for the rate of increase in relative brightness of the filament $\frac{1}{B}\frac{dB}{dt}$ is obtained when account is taken of the relation between brightness and temperature,

$$\frac{B}{B_m} = \left(\frac{T}{T_m}\right)^{\theta} \tag{13}$$

in which θ may be considered constant for values of T/T_m nearly equal to unity. There follows

$$(14) \qquad \frac{1}{B}\frac{dB}{dt} = \theta \frac{1}{T}\frac{dT}{dt}$$

Substitution of $\frac{dT}{dt}$ from (11) in (14) and the elimination of T/T_m by means of an expansion of (13) give

$$(15) \qquad \frac{1}{B}\frac{dB}{dt} = Q \frac{B_m - B}{B_m}$$

Thus it appears expressing brightness in terms of the maximum, that the rate of increase in brightness in the neighborhood of that maximum is also proportional to Q. Similarity of heating curves suggests, in comparing the speeds of various lamps over any fixed relative brightness range, that while (15) would not hold, the deviations for the different lamps would be found approximately the same, and that the function Q would still serve for comparison purposes; for instance, that

$$(16) \qquad Q\,(t_{.7} - t_{.2}) = \text{constant (approx.)}$$

That the function Q, one involving only steady current measurements of wattage, resistance and temperature, in the neighborhood of the maximum temperature of a flash, together with the thermal capacity of the filament, thus involving no candlepower considerations directly, should give the cue to the flashing speed from the light standpoint is on first thought somewhat surprising.

To what extent (16) may be used in representing the results computed on a rigid basis may be seen by referring to Table III. Inspection of the table shows approximate constancy in the product $Q(t_{.7} - t_{.2})$ first with change in the maximum temperature of the flash and second with change in resistance external to the flashing lamp, and third with change in the atmosphere surrounding the filament. Insofar as there is agreement, or lack of agreement, between the experimental and the computed speeds shown in Table II and Fig. 6, there is also agreement or failure on the part of equation (16) in representing actual speed data. Evidently, in a very real sense, the function Q gives the cue to the flashing speed of the lamp and may well be considered the speed function. Different lamps may reasonably be rated as to their flashing speeds through their corresponding Q's.

COMPARISON OF VARIOUS SIGNAL LAMPS FROM DIFFERENT VIEWPOINTS.

The question of flashing speed in considering lamps for signalling purposes is not all important. Usually one is concerned with lamps of a specified voltage, a specified average life—say twenty-five hours—and a specified luminous output.

TABLE III.

Data Showing with What Approximation Equation (16) Represents Computed Speeds for Various Tungsten Filament Lamps Under Different Conditions of Operations.

Lamp‡	T	W watts	R ohms	(CM) joules/degree	β	α	$\frac{R-r}{R+r}$	Q 1/sec.	(t_2-t_1) computed	$Q(t_2-t_1)$
A–33.....	3000°K.	136.5	2.016	0.0216	4.40	1.20	1.00	11.80	0.120 sec.	1.42
	2667	81.1	1.753	.0205	4.52	1.20	1.00	8.49	.167	1.42
	2667	81.1	1.753	.0205	4.52	1.20	.71	7.95	.184	1.44
	2667	81.1	1.753	.0205	4.52	1.20	.00	4.92	.327	1.61
	2232	35.30	1.412	.0190	4.73	1.20	1.00	4.93	.295	1.45
	1800	12.37	1.095	.0175	4.99	1.20	1.00	2.43	.619	1.50
S–142–Ar	3000	80.7	5.78	.00452	3.443	1.225	.74	35.9	.0547	1.42
	2667	54.3	5.01	.00429	3.315	1.225	.70	19.8	.0712	1.41
	2232	30.5	4.03	.00397	3.122	1.225	.65	13.4	.1063	1.43
	1800	16.0	3.09	.00365	2.888	1.225	.56	8.85	.170	1.50
S–142–N	3000	90.3	5.78	.00452	3.28	1.213	.74	27.9	.0504	1.41
S–153–H	2667	243.8	5.01	.00429	4.33	1.225	.72	111	.0157	1.72
	2478	184.1	4.58	.00416	3.65	1.225	.68	80	.0173	1.58
	2232	133.3	4.03	.00397	2.65	1.225	.64	51.6	.028	1.45
S–140–Ar	3000	33.5	70.4	.000393	2.08	1.20	1.00	11.9	.0114	1.36
	2232	15.0	49.4	.000346	2.37	1.20	1.00	69.4	.0192	1.33
	1973	11.23	42.6	.000329	2.22	1.20	1.00	59.3	.0231	1.36
59L.....	3000	13.15	3.31	.000247	4.01	1.35	.79	90	.0165‡	1.48
80S.....	2980	11.07	3.04	.000331	3.42	1.33	.92	52	.0290†	1.51

‡ *Descriptions of these lamps follow:*

Lamp	Filament shape	Filament diameter	Dimensions length	Atmosphere	Cooling due to supports
A–33.....	Straight wire	0.258 mm.	10.85 cm.	Vacuo	None.
S–142–Ar....	Straight wire	0.134	8.5	A at 600 mm.	Present.
S–142–N....	Straight wire	0.134	8.5	N at 600 mm.	Present.
S–153–H....	Very openly coiled wire....	0.134	8.5	H at 600 mm.	Present.
S–140–Ar....	Straight wire	0.039	8.2	A at 600 mm.	Present.
59L.....	Very openly coiled ribbon..	0.021 0.19	1.65	A at 600 mm.	Present.
80S.....	Very openly coiled wire....	0.083	1.65	N at 600 mm.	Present.

‡ Average of two observations.
† Average of six observations.

Most of the data and discussions herein have referred to filaments of a definite size. But now, with a knowledge of the approximate constancy expressed in equation (16), of the life of a filament as a function of its temperature and of its surrounding atmosphere, and of the gas losses in different gases as a function of the filament dimensions, it is possible to determine the flashing speeds of any sized filament for probable conditions of operation. Thus Table IV gives first the characteristics of a single filament

of tungsten operated in various atmospheres at a fixed temperature, and, second, the characteristics of varying sized filaments in the same atmospheres operated under conditions to produce the same luminous flux, the same average life and the same specified voltage. The computations involved while simple in theory are quite tedious. Of course the exactness of the values recorded depends upon the correctness with which the relations used repre-

TABLE IV.

Characteristics of Lamps Containing Tungsten Filaments in Various Atmospheres Computed for Conditions—(A) filament dimensions and maximum temperature constant; (B) lamp voltage, luminous flux and life constant.

Condition	A				B			
Atmosphere	Vacuum	*A* at 600 mm.	*N* at 600 mm.	*H* at 600 mm.	Vacuum	*A* at 600 mm.	*N* at 600 mm.	*H* at 600 mm.
Temperature in degrees K.	2800	2800	2800	2800	2725	3070	3050	2990
Filament length in centimeters	8.24	8.24	8.24	8.24	6.21	2.96	2.90	2.16
Filament diameter in mm.	0.134	0.134	0.134	0.134	0.098	0.073	0.079	0.134
Voltage	14.65	18.45	19.7	39.55	12	12	12	12
Wattage	40.4	64.0	73.0	294	19.7	19.8	23.8	100
Current in amperes	2.755	3.47	3.70	7.44	1.64	1.65	1.98	8.3
Luminous flux in lumens	747	747	747	747	322	322	322	322
Efficiency in $\frac{\text{lumens}}{\text{watt}}$	18.5	11.7	10.4	2.54	16.35	16.3	13.5	3.22
E_t / E_0	1.00	1.58	1.81	7.3	1.00	1.66	1.95	7.67
Life in hours	12.7	1110	890	254	25	25	25	25
α	1.22	1.22	1.22	1.22	1.22	1.22	1.22	1.22
β	4.48	3.37	3.42	4.79	4.51	3.21	3.42	5.40
C in $\frac{\text{degrees}}{\text{joules}}$	.00439	.00439	.00439	.00439	.00173	.00485	.00557	.00109
Q in $\frac{1}{\text{sec.}}$	18.7	2.39	27.6	144	23.9	59.8	65.0	203
$Q(t_1-t_2)$	1.42	1.42	1.42	1.42	1.42	1.42	1.42	1.42
(t_1-t_2) in sec.	.076	.059	.052	.010	.059	.024	.022	.0070

sent facts. Inasmuch as the signalling type of incandescent lamp differs greatly in fundamental principles of construction from ordinary commercial lamps, it naturally follows that much of the data upon which Table IV is based has not been subjected to repeated thorough tests. To illustrate, considerations of speed and of covering a desired field when used with a mirror for directing the flux into a beam, may require very open coils of the filament in the signal lamp in contrast with the tightly closed coils of ordinary lamps. The effect of this on gas-loss data is evident:

the effect on life considerations, while not so evident, is possibly just as real.

The writer has assumed in computing results given in Table IV that the life of very open coiled or straight filament lamps to depend solely on the rate of vaporization, as is the case for commercial, straight-filament, vacuum lamps. A meagre reference by Mackay [7] on the relative decrease in the vaporization of tungsten in a nitrogen atmosphere, some data obtained in the Research Laboratory at Schenectady on a comparison between argon-filled and nitrogen-filled lamps, and some simple life tests conducted by the writer's colleague, Dr. C. F. Lorenz, have led the writer to conclude that atmospheres of nitrogen and of commercial argon at 600 mm. pressure reduce the rates of vaporization of tungsten filaments immersed in them to respectively about one-seventieth and one-ninetieth of the rate in vacuo. Or what is the same, the lives of lamps with filaments immersed in these atmospheres will be about 70 and 90 times as long as the lives of lamps with filaments in vacuo. As to the life of a tungsten filament in a hydrogen atmosphere, there is much greater uncertainty. Little is known beyond the fact that it is much less than that for the same filament at the same temperature in argon or nitrogen. Assuming the rate of vaporization to depend on the diffusion of the tungsten vapor away from the filament, the application of the diffusion theory due to Stefan and Winkelmann,[8] leads to a life in hydrogen equal to about two-ninths of that in argon. We shall probably not be far from the truth by assuming, as we have here, the life of a given filament at a given temperature in vacuo, in argon, in nitrogen, and in hydrogen to vary as 1 : 90 : 70 : 20. For the variation in the rate of vaporization of tungsten in vacuo with temperature, the results of the classic investigation of Langmuir's [9] corrected to the scale of temperature [10] now generally accepted have been used. His results thus corrected are given fairly closely by the equation

$$(17) \qquad \log m = 21.56 - \frac{47570}{T} - 3.30 \log T$$

where m represents the rate of vaporization in grams per cm.^{2} per

[7] *Trans. I. E. S.*, Sept., 1914, p. 745.
[8] Winkelmann, "Handbuck der Physik," I, p. 1429.
[9] *Phys. Rev.*, **2**, p. 329, 1913; *Phys. Rev.*, **10**, p. 377, 1917.
[10] *Gen. Elec. Rev.*, **20**, p. 819, 1917.

second. This is connected with actual life data through the commercial experience that the 60-watt, 110-volt, vacuum lamp—diameter of 0.050 mm.—at 2440° K has a life of 1000 hours.[11]

For the gas losses from small filaments for use in compiling Table IV, the writer has taken his own data. Defining E as the rate of dissipation of energy per unit of surface area and thus including gas losses together with radiation, it has been found that the results obtained may be expressed with considerable exactness over the temperature range 1800° K to 3000° K by empirical formulæ of the type.

$$E = A + B\,(\log T - 3.3) + C\,(\log T - 3.3)^2 \tag{18}$$

The constants A, B and C for a given atmosphere depend on the diameter of the filament. Values for a filament diameter of 0.134 mm. are given in Table V for various atmospheres. Given

TABLE V.

Values of the Constants A, B and C of Equation (18) Consistent with Expressing E in Watts per Square Centimetre for a 0.134 mm. Cylindrical Tungsten Wire in Various Atmospheres. Due to Disregarding the Thermal Expansion of the Filament, E is Really Expressed in Watts per Square Centimetre of Filament Surface as Measured at Room Temperature.

Atmosphere	A	B	C
Vacuum	1.379	4.87	1.40
Argon (commercial) at 600 mm. pressure	1.792	3.00	1.25
Nitrogen at 600 mm. pressure	1.859	2.83	2.00
Hydrogen at 600 mm. pressure	2.458	1.61	10.8

E as a function of T for one filament diameter for a given atmosphere, a corresponding value for a filament with another diameter in the same atmosphere may be readily obtained by the following empirical relation which holds fairly well for filaments varying in diameter from 0.03 mm. to 0.3 mm.

$$\frac{\left[\frac{E_a}{E_v} - 1\right]_1}{\left[\frac{E_a}{E_v} - 1\right]_2} = \left[\frac{d_2}{d_1}\right]^x \tag{19}$$

where E_a and E_v correspond respectively to a filament in a gaseous atmosphere and in a vacuum and d the filament diameter. For

[11] This in reality represents a rated life which is noticeably less than the experienced life. No material error in argument is introduced by this assumption of equality.

argon and nitrogen x approximates 0.70 for hydrogen 0.75. Equation (19) states in general terms that the gas losses vary inversely as the 0.7 or 0.75 power of the filament diameters.

Other necessary data [12] used in compiling Table IV are well known, or are such as may be obtained from a consideration of what has been given already. The cooling effects of filament supports, which may be considerable in very low-voltage lamps, have been ignored here. It is probable that the values of $(t_7 - t_2)$ computed for the hydrogen lamps are too small because of ionization effects.

A study of Table IV suggests certain general laws applicable to flashing signal lamps which, while not proven, may be shown to be true.

(1) For a given filament operated in various gases, including in vacuo at a fixed maximum temperature, the flashing speed is greatest in that lamp for which the gas loss is greatest.

(2) For cylindrical filament lamps of the same open construction possessing the same luminous flux and life on a specified voltage, the flashing speed is the greatest in that lamp for which the gas loss is greatest.

(3) For cylindrical filament lamps of the same open construction possessing the same luminous flux and same life when operated at some fixed voltage, the efficiency of the vacuum lamp is less than that of the gas-filled lamp for large sized filaments. The reverse is true for small-sized filaments. In condition *B*, Table IV, the efficiency of the vacuum lamp is greater than that of the nitrogen or the hydrogen lamps, and very nearly the same as that of the argon lamp. For a slightly larger filament the reverse would be true for the argon lamp.

(4) For cylindrical filament lamps of the same open construction possessing the same luminous flux and the same life on a specified voltage, the filament is shortest in the lamp possessing the greatest gas loss. This consideration is of importance in lamps which are used with mirrors or lenses to give intensified beams, in that the longer the filament the more effectively may one cover a certain field or area containing the observer to whom signals are sent.

[12] Worthing: *Phys. Rev.*, **10**, p. 377, 1917; **12**, p. 199, 1918; *Bul. A. I. M. and M. E.*, Sept., 1919; Hyde, G., *E. Rev.*, **20**, p. 819, 1917; Hyde, Cady and Forsythe, *Phys. Rev.*, **10**, p. 819, 1917.

(5) For cylindrical filament lamps of the same open construction possessing the same luminous flux and the same life on a specified voltage, the temperature is lowest in the vacuum lamp and highest in that gas-filled lamp which has the least gas loss. This may be of importance where the color of the light is a factor.

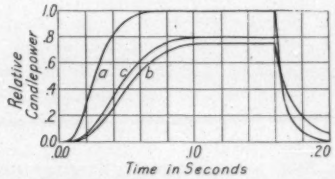
RIBBON FILAMENTS VS. WIRE FILAMENTS.

For equal radiating surfaces a ribbon filament possesses a much less mass of material to be heated than does an equivalent wire filament and therefore will inherently respond the more rapidly on flashing. The flashing speed of a given ribbon filament in vacuo is quite closely equal to that of a wire filament whose diameter is twice the thickness of the ribbon, as follows directly from considering the ratios of the surfaces of the filaments to their masses. Lack of actual equality in gas-filled lamps is due to a difference in gas loss. The great desirability of a ribbon filament in signal lamp construction depends on the fact that through thinness any desired flashing speed is obtainable and that through variations in width any desired current-carrying capacity. A ribbon filament combines the current-carrying capacity of a large wire filament with the high speed of a small wire filament. Contrasting wire and ribbon filaments of the same current-carrying capacity operated at the same temperature. We find that considerations of life are unfavorable to the ribbon filament. Vaporization of the filament material at a given rate in a given length of time produces a greater relative change in the mass of the ribbon filament than in that of the equivalent wire filament. We therefore expect to operate the ribbon filament at a reduced temperature. However, as an offset to this, the ribbon form may possibly be favored somewhat in the vaporization rate and in the gas loss due to the lines of flow of vapor and of heat being on the whole parallel near the ribbon filament in contrast to the spreading lines of flow about the wire filament. A few careful measurements which have been made indicate an appreciable factor in favor of the ribbon form in cutting down gas losses. However, the great advantage of a ribbon form, considering everything, is the possibility offered by the ribbon filament in increased efficiency without loss of speed by changing from a gas with a great gas loss to one with a small gas loss. Thus it was felt, in planning to meet the demands for a 6-volt, 2-ampere lamp for warfare, that a

proposed lamp containing a wire filament should be filled with nitrogen, while the ribbon filament lamp might be filled with argon. Flashing speeds for preliminary lamps of these two types from which the final selection was made, No. 26L, No. 59L, and No. 80S, which illustrate these deductions have already been referred to in Tables I and III.

No speed tests were carried out with 6-volt, 2-ampere signal lamps with ribbon and wire filaments operating at temperatures such as to yield a 25-hour life. However, starting with the curve of Fig. 3 and the speed data of 59L and 80S, given in Table III, it is not difficult to tell what such curves will be like. Fig. 7 shows what is to be expected for the two types as well as for a ribbon

FIG. 7.



Expected speed of performance for three 6-volt, 2-ampere tungsten-filament signal lamps operated at temperatures corresponding to about 25 hours of life. *a*. 0.021 mm. ribbon filament in an argon atmosphere. *b*. Ribbon filament of the same thickness in vacuo. *c*. 0.084 mm. wire filament in a nitrogen atmosphere. The cooling curve for the wire-filament lamp (not shown) lies generally near the cooling curve of (*a*). The corresponding maximum temperatures are approximately 3020°K., 2660°K. and 3050°K.

in vacuo. (Due to neglecting end-coolings in Tables IV, some discrepancies will be found between the data there given and that represented in this figure.) The advantage of the ribbon filament in argon over the wire filament in nitrogen in flashing speed is seen to be approximately 1.6, in luminous efficiency 1.25. The reason for the actual selection of lamps with ribbon filaments in argon for warfare signalling is apparent.

It is interesting to note certain tests conducted by the writer's colleague, W. E. Forsythe.[13] Using sometimes a special sectored disk, so cut as to give at will various combinations of dot-and-dash signals when rotated before a steady light source, and at other times a special commutator for producing at will any one of the same combinations of dots and dashes by flashing a signal lamp, he found, using 6-volt, 2-ampere lamps, (1) that the maxi-

[13] *Phys. Rev.*, 16, p. 62, 1920.

mum speed of reception of signals using signal lamps with ribbon filaments in argon did not differ noticeably from that using the rotating sector and a steady source, which presumably offers the maximum possible speed; (2) that the speeds of reception of signals were noticeably greater when using lamps with ribbon filaments in argon than when using lamps with the same filaments in vacuo; and (3) that the speeds of reception of signals were noticeably greater—roughly of the order that might be expected from Fig. 7—when using lamps with ribbon filaments in argon than when using lamps with wire filaments in nitrogen.

CONCLUSION.

The selection of a lamp for signalling purposes which shall have a given life and luminous flux at a specified voltage naturally depends on various factors such as the rapidity of the flash, the size and the intensity of the beam from the unit of which the lamp is a part, the luminous efficiency of the lamp either for all visible wave-lengths or for some limited region of the spectrum, and the ruggedness of structure. Certain factors will naturally be of greater importance than others and may be decisive in making a selection. So far as speed and efficiency are concerned, what has been said indicates clearly that a lamp containing a ribbon filament in argon represents the preferred type of construction for use in a 6-volt, 2-ampere signalling unit. In a future paper entitled "The Theory of Signalling Units Employing Incandescent Lamp Sources" the author intends to discuss the characteristics of the beam from a signalling unit.

The writer is greatly indebted to Mr. Kenneth Moorhead who has assisted throughout the investigations, particularly in the making of the speed measurements.

CLEVELAND, OHIO,
November, 1920.

American Beet Sugar. (*Sugar*, December, 1920, p. 690.)—American beet sugar is expected to harvest a larger California crop this year, according to present indications. Its coast campaign has just been completed with satisfactory results and about 20 per cent. of its full outturn produced in the Rocky Mountain States, yielding 100,000 bags more than in 1919–1920. Indications are that its total output this year will be between 1,400,000 and 1,500,000 bags, against 1,077,000 for the previous campaign.

Progress in Commercial Aviation.—In an address before the Society of Automobile Engineers, in New York, on Tuesday, January 11, 1921, Grover C. Loening asserted that misdirected aviation development is largely responsible for the present condition of aeronautics in the United States. On the basis of the experience of the past few years, it appeared that the supposed advantages of multi-engined and all-metal planes have been important causes of false leads in the development of commercial service. Mr. Loening claimed that the useful loads per horsepower are almost as great in a single-engined plane as in one equipped with two or more engines. He declared that it is a mistake to assume that a duplication of engines gives greater safety from engine failure, since most of the causes of failure, such as weather conditions, sleet and ice, would stop all the motors. He also said that it is very rare that the engine fails in itself. Something usually fails in the gas line or the water line. Engines applicable to war-planes are not suitable for commercial planes. The following were given as desirable features in the development of the power-plant in commercial planes. (1) Muffling devices. (2) Geared-down engines, or, better still, slower running engines to improve the propeller power, particularly in starting and climbing speeds. (3) Further development of the reversible pitch propeller.

Before the same society Professor E. P. Warner presented a paper which included some statistics of the passenger service between England and the continent. In the first eleven months of the service there was a total of twenty-four accidents, in four of which one or more persons were killed. The pilot was killed in each case, but only one passenger in the entire period. The average death-rate for pilots was one for every 2410 hours in the air. The passenger rate is one death for every 67,000 carried, and taking into consideration the fact that the average speed is 90 m.p.h., one fatality for every 1,640,000 passenger miles.

H. L.

Prickly Pear Oil.—In the manufacture of an edible jelly, known as *queso*, from the fruit of the prickly pear, the seeds are discarded as waste. These seeds are rich in oil; the seeds of a variety of white prickly pear, known as *tuna blaca de huerta*, contained 10.89 per cent. of oil. By extraction of the seeds with petroleum ether, the oil was obtained as a greenish-yellow, odorless, somewhat viscous oil. Among its constants were: Acid value, 3.09; saponification number, 189.5; iodine number, 116.3; Reichert Meissl number, 2.8; Hehner number, 93.81. From the results of his study, S. LOMANITZ (*Journal Ind. and Eng. Chem.*, 1920, xii, 1175) concludes that this oil should probably be placed among the semi-drying oils, and might be used in the arts if produced in sufficient quantity.

J. S. H.

THE APPARENT FORM OF THE SKY-VAULT.*

BY

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THE apparent form of the vault of the sky has attracted the attention of many investigators for centuries. Alhazen, an Arab astronomer, wrote about it in the tenth century, and since that time hundreds of memoirs upon the subject have appeared in technical and scientific literature. Notwithstanding all the investigations there is no general agreement as to the cause for the illusion of a flattened dome of sky; however, there is a general agreement that the vault of the sky usually appears somewhat flattened. Although the evidence which the writer will submit may not be conclusive, in his opinion it points very strongly toward the chief cause of the illusion.

Before presenting this evidence it may be of interest to discuss some of the pertinent details and some of the results obtained by other investigators. Dember and Uibe assumed the apparent shape of the sky-vault to be a part of a sphere (justifying this assumption to their own satisfaction) and obtained estimates of the apparent depression at the zenith. They estimated the middle point of the arc from the zenith to the horizon and then measured the angular altitude of that point. They found that the degree of clearness of the sky has considerable influence upon the apparent height and they state that the sky appears higher in the subtropics than in Germany. On very clear nights they found that the shape of the sky-vault differed little from that of a hemisphere. They concluded that the phenomenon is apparently due to optical conditions of the atmosphere which have not been determined.

Nearly two centuries ago Robert Smith and his colleagues concluded that the sky appeared about three times as far away at the horizon as at the zenith. They also determined the relative apparent variation of the size of the sun with altitude and suggested that the illusion of greater size of the sun near the horizon was due to the illusion of the flattened dome of the sky. They

* Communicated by the Author.

also made similar measurements for the moon and certain constellations. The apparent size of these heavenly bodies according to their measurements was three or four times greater at the horizon than at the zenith.

Photographs have been published of the sun and of the moon at various altitudes which prove that the apparent enlargement of these heavenly bodies near the horizon is an illusion. The writer recently confirmed this by recording the paths of these bodies on panchromatic photographic plates, using a red filter to minimize the effect of the selective absorption of the atmosphere.

The appearance of the flattened vault of the sky is held by some to account for the apparent enlargement of the sun, moon, and constellations near the horizon. That is, they appear more distant at the horizon and we instinctively appraise them as being larger than when they are at higher altitudes. Aerial perspective is often considered to be a contributing factor. Distance is often estimated by the definition and color of objects seen through great depths of air. Distant objects are blurred by the irregular refraction of the light-rays through non-homogeneous atmosphere. They are also obscured to some degree by the veil of brightness due to the illuminated dust, smoke, etc. They are also tinted by the superposition of a tinted atmosphere. Thus we have "dim distance," "blue peaks," "azure depths of sky," etc., represented in photographs, paintings, and writings.

We judge unknown size by estimated distance and unknown distance by estimated size. If we unconsciously think of the path of heavenly bodies as being along the surface of a flattened vault of sky it is obvious that we must unconsciously think of them being farther away at the horizon than at the zenith. Therefore, the necessary compensation must be obtained in some manner and it may be that it manifests itself in an appearance of greater size at the horizon. Certainly these heavenly bodies universally appear considerably larger at the horizon than at higher altitudes. It is also certain that this is largely if not entirely an illusion.

The writer has had an excellent opportunity to study the apparent form of the sky-vault during many high-altitude flights in airplanes. The brevity of the interval of time that elapsed between views at the ground, in the earth-haze and low-cloud region, and at high altitudes where the sky was dark, was an ideal condition for making these observations.

The sky is bright, due to scattering of light by actual particles of solid matter and moisture and possibly by molecules of gas. If the region above the earth was a void as it is in interstellar space, the sky would be black in the daytime and the sun would appear more piercingly bright. Shadows would generally be very harsh and dark. Lack of optical homogeneity of the atmosphere due to varying refractive index is likely to be partially responsible for the brightness of the sky. Usually a prominent layer of haze about a mile in thickness (although this varies considerably) lies next to the surface of the earth. The top of this haze is fairly well-defined and cumulus clouds project above it like partially submerged icebergs. If there are no high clouds present the sky when seen above the earth-haze is deep blue, but still appears fairly bright near the horizon. After an altitude of four or five miles is reached most of this thin upper haze is left behind, and the sky is often very dark and the sun is piercingly bright. Usually there is little or no bright haze adjacent to the sun at these high altitudes as is commonly seen from the earth's surface.

With these brief glimpses of the aspects of the sky as one ascends, let us resume our view of the sky from the earth's surface when cumulus clouds are present. The bases of these clouds are fairly flat because they are at the level where the air is saturated. This level varies in altitude from three to five thousand feet. These clouds, if they cover the sky completely, form a flat ceiling, but the latter appears to bend down at the horizon. When cumulus clouds are present here and there they appear like a few stray pieces of fleecy wool overhead, but toward the horizon they appear *en echelon*, stepping down toward the earth and meeting it at a distance which appears many times greater than their vertical distance overhead. This can account for the appearance of a very much flattened vault of sky.

This apparent shape persists to some degree even in clear weather, perhaps partially on account of the degradation of color toward the horizon but chiefly to the variation in brightness. Usually the sky is considerably brighter near the horizon than at the zenith, and the latter being darker appears to hang low.

Now let us ascend rapidly in an airplane or a balloon on a day when the illusion of the flattened sky-vault is quite powerful, such as on a day when many cumulus clouds are in the sky. We leave the earth with a strong impression of a flattened vault of clouds and

haze above us. We see it bending to meet the horizon on all sides. In a few minutes we are on the same level as the clouds and low-lying haze and we are surprised to find these are levels and do not comprise a vaulted roof. Notwithstanding the many flights which the writer has taken above this level, he still experiences a feeling of mild surprise at this revelation. This testifies to the persistence and strength of the illusion.

After we have nosed our way up through the low cloud-and-haze level, we find another horizon and another sky-vault. Assuming there are no upper clouds present, we see a fairly dark blue sky at the zenith but which brightens and becomes less saturated in color toward the haze-horizon. Under such conditions the sky-vault now appears more like a hemisphere than the very much flattened vault it appeared to be when viewed a few minutes before from the earth. However, it still appears somewhat flattened at the zenith. But as we continue to climb we leave more and more of the "sky" behind us. The sky above grows darker gradually until at an altitude of four miles it may be only one-fifth as bright as it is on an unusually clear day as seen from the earth. Now it appears like a hemispherical dome and really there are times when one is not conscious even of the dome. That is, there are times when this deep blue is merely an infinite space of nothingness.

In the course of a few minutes we have seen two sky-vaults, and the brevity of this interval permits almost a direct comparison of the two. Such a comparison is unobtainable by any other means than aerial travel. The suddenness of the transition from the powerful illusion of a flattened vault of sky to a much weaker illusion of a nearly hemispherical dome is very convincing. After flying in the upper region and viewing the level sea of haze meeting the horizon in an unbroken circle, let us suddenly dive downward through this level. In a minute we are again viewing the haze-and-cloud level from the lower side and are seeing the clouds again *en echelon,* stepping down to the earth level and meeting at the horizon.

The writer has repeated these experiences many times under vastly different sky-conditions and always with the same impressions. However, the apparent flattening of the sky-vault varies considerably, depending upon the conditions of clearness, haziness, or cloudiness. These variations provide opportunities for studying this illusion under many conditions, but best of all is the

kaleidoscopic change witnessed during a rapid ascent and descent. The writer is thoroughly convinced that the apparent flattening of the sky-vault is due to such conditions as the appearance of clouds *en echelon*, the gradual variation in brightness and color of the sky from the zenith to the horizon, and the apparent lowness of a darker zenith. A very dark uniformly overcast sky, a uniformly bright, hazy sky, and a uniform blue sky as seen at high altitudes, approach in appearance a hemispherical vault. An appearance of flattening is encountered on clear days when there is a gradual change in the brightness and color of the sky. The appearance of greatest flattening is found on cloudy days such as those on which many small cumulus clouds are present.

That the apparent enlargement of heavenly bodies near the horizon is almost entirely, if not entirely, an illusion, appears to be fully proved. These striking experiences with the persistency and powerfulness of the illusion of the flattened sky-vault lead the author to believe that the apparent enlargement of heavenly bodies is at least partially due to it. But in discussing this other illusion many peculiar conditions and prejudices must be taken into account. For example, if various persons are asked to give an idea of the size of the disk of the sun or moon, their answers would vary usually with the head of barrel as a maximum. However, the size of a tree at the sky-line might be given as thirty feet. At the horizon we instinctively compare the size of the sun, moon, and constellations with hills, trees, houses, and other objects (seen in front of them), but when the former are high toward the zenith in the empty sky we may judge them in their isolated position to be nearer, hence smaller.

Preparation of Pure Carbon Dioxide.—ROBERT CROSBIE FARMER, of the Royal Arsenal, Woolwich, prepares carbon dioxide completely free from air by the reaction between potassium hydrogen carbonate and sulphuric acid. Carbon dioxide is passed through a solution of potassium hydrogen carbonate (300 grams to the litre) and also through a solution of sulphuric acid (120 c.c. diluted to 1 litre); the solutions are thus rendered free from dissolved air; they are then caused to react in an air-free vessel; and pure carbon dioxide, entirely free from air, is obtained. The product is so pure that it gives practically no gaseous residue on absorption with potassium hydroxide solution (*Journal of the Chemical Society*, 1920, cxvii, 1446–1447).

J. S. H.

Results and Analysis of Magnetic Observations During Solar Eclipse, May 29, 1919. LOUIS A. BAUER. (*Terrestrial Magnetism and Atmospheric Electricity*, September, 1920.)—This eclipse afforded favorable opportunities for studying "solar-eclipse magnetic variation" not only near the magnetic equator but also in both magnetic hemispheres. After the observations then made "there cannot be any doubt that the earth's magnetic condition is subject to an appreciable magnetic variation during a solar eclipse. Indeed, the greater surprise would be, in view of the existence of the solar-diurnal and lunar magnetic variations, if the gradual withdrawal and restoration of solar radiation during a solar eclipse, in greater or less degree, over nearly one-half of the daylight portion of the earth, did not give rise to a magnetic variation."

Happily, May 28th, 29th, and 30th were magnetically calm, so that the effects of the eclipse were projected upon a colorless background. The maximum change of declination was observed at Sobral, Brazil, where the compass needle moved almost three minutes of arc farther toward the east. The maximum change of inclination was at Cape Palmas, Liberia, where the north end of the dipping needle fell two and one-half minutes further below to the horizontal. The changes in declination and horizontal intensity were about such as would have been produced by a north magnetic pole located in the shadow cone cast by the moon.

G. F. S.

Gypsum Deposits in the United States. (*U. S. Geological Survey Press Bulletin No. 460*, December, 1920.)—A bulletin describing the gypsum deposits in the United States has just been issued by the Survey. Gypsum is the rock used for making plaster of Paris and hard wall plaster, and it is also an ingredient of Portland cement and is used as a fertilizer. The bulletin shows that gypsum is distributed from New York to California and from Michigan to Texas. The deposits in some States are so small that they may be worked out in a few years; those in other States, like Wyoming and New Mexico, consist of thick beds that crop out at the surface for hundreds of miles and that are seemingly inexhaustible. The bulletin contains 325 pages and many illustrations and includes a technical discussion of the physical and chemical properties of gypsum, a classification of the deposits by origin, a history of the gypsum industry in the United States, and a brief description of processes of mining and milling, as well as a bibliography, but it consists principally of descriptions of the deposits, by States, written by State geologists and others who are thoroughly familiar with them. The book, which is published as Bulletin 697 of the U. S. Geological Survey, was compiled and in part written by R. W. Stone, a geologist who has made a special study of gypsum.

NOTES FROM THE U. S. BUREAU OF STANDARDS.*

THE MAGNETIC RELUCTIVITY RELATIONSHIP AS RELATED TO CERTAIN STRUCTURES OF AN EUTECTOID CARBON STEEL.[1]

By C. Nusbaum, W. L. Cheney and H. Scott.

[ABSTRACT.]

THE magnetic reluctivity (ρ), defined as the ratio of the magnetizing force to the induction, has been shown by Kennelly to be related to the magnetizing force by the relationship

$$\rho = \alpha + \beta H, \tag{1}$$

but for high inductions this has to be modified to

$$\rho_0 = \frac{H}{B - H} = \alpha + \beta H, \tag{2}$$

where ρ_0 is the metallic reluctivity and $B - H$ is the metallic induction or flux carried only by the molecules of the metal. For pure and well annealed materials the reluctivity line is a straight line, while in the more or less impure commercial materials the reluctivity line, though approximately a straight one, has generally a point where its slope changes. Since the change in the slope of the line is in general greater with the increase in impurity of the material, the cause is evidently a lack of homogeneity, *i.e.*, the presence in the substance as aggregates or inglomerates of materials of different magnetic characteristics. Although the arrangement of the constituents in a carbon steel is generally a random one, it may be considered as combinations of any of the three simple arrangements, *viz.*: (*a*) the parallel, (*b*) the series, and (*c*) the spheroidal.

In the experiments described in the present paper, two specimens of an eutéctoid carbon steel (0.85 per cent. carbon) were selected and turned down to a uniform diameter of approximately

* Communicated by the Director.

[1] Scientific Paper No. 404.

7 mm. Each of these specimens was quenched from 800° C., one in oil, the other in water, and then carefully ground down to 6 mm. Each specimen was then cut in halves designated A and B, which were then drawn alternately to increasingly higher temperatures up to 700° C. Normal induction curves up to values of the magnetizing force as high as 2500 gausses were determined after each operation.

Curves for a few of these heat treatments are shown. Other magnetic properties shown graphically are (*a*) the values of the induction for constant values of the magnetizing force as plotted against the drawing temperatures, (*b*) the reciprocals of the susceptibility (4π times the reluctivity) as plotted against the magnetizing forces, (*c*) the value of the saturation intensity of the magnetization as plotted against the drawing temperatures, and (*d*) the values of the "magnetic hardness" as plotted against the drawing temperatures. Referring to equation (2), the values of the saturation intensity of magnetization are equal to $\frac{1}{4\pi\beta}$, *i.e.*, the reciprocal of the slope of the reciprocal of susceptibility line. The values of the "magnetic hardness" are the values of α, *i.e.*, the intercept on the axis of ordinates.

These two characteristics are those with which this paper is most concerned, since they show more than any others the transformations which take place in the steel as a result of the heat treatment. It is found that in a region included by the quenched condition and a drawing temperature of 230° C., in which the specimen is known to be martinsitic in structure, there is a distinct bend in the reluctivity line, and consequently there are two values of the saturation intensity of magnetization and the "magnetic hardness" as calculated from the upper and lower portions of the reluctivity line. In the range of drawing temperatures bounded by 230° C. and 470° C., in which the steel is troostitic, the reluctivity line has but one slope, hence the saturation intensity of magnetization and the "magnetic hardness" each have but one value for a given drawing temperature and the material is magnetically homogeneous. Beyond 470° C. the reluctivity line again has a bend and the material is non-homogeneous, this inhomogeneity being due to the increasing size of the aggregates and to their approaching stratification.

ANNUAL REPORT OF THE DIRECTOR OF THE BUREAU OF STANDARDS.[2]

[ABSTRACT.]

The annual report of the Director of the Bureau of Standards for the fiscal year ended June 30, 1920, contains some valuable and interesting information.

During the year the work of the Bureau has undergone readjustment of staff and work. Naturally the research for the military departments has considerably diminished, though not as much as had been anticipated; while work for the industries has increased to a very great extent. During the year the Bureau completed 106,899 tests of weights, measures, measuring instruments, mechanical appliances and materials.

During the war American manufacturers were brought into closer contact with the Bureau than ever before, and this relationship has continued, with the result that many industries now look to the Bureau for aid in the solution of their problems. The volume of research results made available for the industries is evidenced by the 106 new publications issued during the year giving the results of the scientific and technical investigations and researches of the Bureau.

The regular appropriations of the Bureau for the fiscal year 1920 amounted to $1,397,260; and additional items of $495,000 were carried in the first Deficiency Appropriation Act, making a total of $1,892,260. Some reimbursements were received from other departments for coöperative researches, although not in the same volume as during the war period. The total disbursements during the year amounted to $1,686,345.56.

The staff of the Bureau included 382 statutory employees and about 600 engaged in research investigations specially authorized by Congress. Of this number, 211 were scientific positions, 55 office assistants, 76 engaged in the operation of plant, and 40 in construction work.

The salaries paid to the employees of the Bureau are still inadequate, and because the Bureau can not successfully compete with the salaries paid by industrial concerns, there was an excessively large labor turn-over during the fiscal year. It is hoped that this condition will be improved during the coming year, as

[2] Miscellaneous Publication No. 44.

it is extremely difficult to maintain high-grade scientific work on a first-class basis with a constantly changing personnel.

The work of research institutions such as the Bureau of Standards is of unusual importance at present because American industries have taken up the manufacture of products which before the war were produced entirely in Europe. As these industries are now engaged in work of this sort on quite an extensive scale, it is essential that they be given every chance to meet fairly the foreign competition which will undoubtedly develop. In order to do this, it is necessary that they be kept informed of all the latest scientific developments in manufacturing processes. Research work of this kind can generally be carried out on a large scale only by some centrally located and well-equipped institution, such as the Bureau of Standards.

BUYING COMMODITIES BY WEIGHT OR MEASURE.[3]

[ABSTRACT.]

THE material in this publication is a reprint from Circular No. 55. All the information in that Circular especially of use in the purchase of ordinary commodities has been included here. The publication explains the Bureau's interest in this subject and gives briefly some of the results of the investigation made by the Bureau upon commercial weights and measures throughout the United States. The best methods of buying commodities and of checking the purchases made are detailed and in this connection apparatus are described comprising satisfactory household test sets and their use in determining whether or not full weight and measures are being received. Abstracts of some useful Federal and State laws are given. One section is devoted to kitchen measuring appliances and capacity units employed. The appendix contains various tables of weights and measures.

STANDARDS FOR GAS SERVICE.[4]

[ABSTRACT.]

THE large demand for the three earlier editions of Circular 32, "Standards for Gas Service," and the favorable comment which they have called forth have clearly demonstrated the value

[3] Miscellaneous Publication No. 45.

[4] Circular No. 32, 4th edition.

of a publication of this kind. Economic conditions, gas-making practice, and the purposes for which gas is used change from time to time with the development of the industry, and with such changes should come changes in the various state and city regulations. To be most valuable, therefore, a publication such as this must be revised from time to time to take cognizance of these new conditions. The three previous editions of this circular were issued in 1912, 1913, and 1915, respectively. The preparation of the fourth edition has been delayed on account of the increased demands upon the Bureau incident to the war.

In this new edition the Bureau presents a very complete résumé of state and city regulations now in force defining gas service, and brings up to date the discussion of technical requirements and the Bureau's recommendations of rules and ordinance forms. In order to take full advantage of the recent experience of members of its staff and of others throughout the United States with whom it has coöperated, it has been found necessary to extend greatly or to wholly rewrite certain sections of this circular. Those who have used the earlier editions are, therefore, urged to note with care the more important portions of the discussion, in order that they may have clearly before them the significance of these additions and changes. It is hoped that this revision will increase the usefulness of the publication.

MEANING OF STANDARDS FOR GAS SERVICE.

In order to insure satisfactory gas service the public authorities have usually found it desirable to establish regulations governing the quality of the gas to be supplied, and setting forth the privileges, duties, and responsibilities of the company in the conduct of its business. These regulations should cover the three general requirements of good service, which are: (1) that gas of satisfactory and reasonably uniform quality and pressure be available to the consumers at all times and that such gas be correctly metered; (2) that the price of gas be reasonable, though adequate to permit the maintenance of the company's equipment at a high state of efficiency and the earning of a fair return on the investment; and (3) that all portions of the municipality or district which are sufficiently populous to warrant it be supplied with gas.

The first of these general requirements defines "Standards for Gas Service," which comprise the conditions which must be

defined in respect to heating value, purity, pressure, and measurement of gas, and the relation of the gas company to its customers. These questions receive the principal consideration in this circular. However, the probable effect of such regulations upon the cost and selling price of gas must be carefully considered, for in general any increase in the cost of manufacturing or supplying gas falls ultimately upon the customers. Therefore, only those rules and regulations should be made which really improve the service enough to justify the cost of meeting them.

In the formulation of service rules and in the enforcement of such requirements it should always be borne in mind that these regulations are really a technical specification covering the quality of the commodity and the service to be supplied under a franchise which is in effect a contract with the people. These specifications should not be looked upon as police regulations of the state or the city, but rather as a part of a business arrangement between purveyor and users of gas, and if properly drawn they will protect the interests of both parties to the contract. To do this they must be not only fair and equitable, but also clear and comprehensive, defining precisely and without ambiguity all the important conditions which it is expected the gas company shall meet in furnishing gas service. The fact that the company is likely without requirement to fulfill certain important conditions is not sufficient reason for the omission of these conditions from the rules or ordinance. And, on the other hand, it is not reasonable or fair to the gas company to omit rules which afford it protection against unreasonable demands or unjust criticism.

HEATING VALUE STANDARDS.

Heating value requirements should not only provide for a certain quantity of heat per cubic foot, but should insure to the consumer a gas of such characteristics that its heat may be utilized conveniently and efficiently. Due consideration must be given to the types of equipment and processes of manufacture in most common use, and to the grades of gas-making materials in use or economically available. These conditions may change from time to time, and a heating value correct at the time of adoption may require change later. The gas should be free from excessive quantities of easily condensible hydrocarbon vapors, since its heating value and composition can then be maintained more nearly

uniform, and a more satisfactory and efficient service to the consumer will result. Ultimate cost to the consumer is of utmost importance. In fact, heating-value regulations should be so fixed as to promote efficiency and good service, or, as it is often expressed in other words, so that the average consumer will do his cooking, heating, and lighting at the least cost and with the least possible cause for complaint. The determination of the best heating value standard cannot, therefore, be made by the use of an empirical formula or by averaging the results actually obtained at the various plants. It must rather be a matter of engineering judgment based on a knowledge of prevailing conditions.

CANDLEPOWER REQUIREMENTS.

Gas was originally used almost exclusively for open-flame lighting, and naturally, therefore, most of the early requirements as to the quality of the gas related to the amount of light produced in such burners, *i.e.*, to the open-flame candlepower of the gas. However, at the present time, cooking, water heating, mantle lighting, and industrial applications of gas consumed by far the larger percentage of the total gas made, and in these operations it is the heat given out in combustion of the gas that is of importance to the user. Only a few per cent. of the gas distributed in this country is used in open flames, and, in fact, probably not over 2 per cent. of it should be so used, considering only economy to the consumer.

As a result of this change in conditions, heating-value requirements have largely replaced candlepower requirements. In fact, the situation has so changed that there is no longer any justification for the adoption of new candlepower regulations.

RECOMMENDED SPECIFICATION FOR ASPHALT VARNISH.[5]

[ABSTRACT.]

THIS specification was prepared under the auspices of the Bureau of Standards by the U. S. Interdepartmental Committee on Paint Specification Standardization, September 27, 1920. The Committee consisted of representatives of the War, Navy, Agriculture, Interior, Post Office, Treasury, and Commerce Departments, the Panama Canal, and the Educational Bureau of the Paint Manufacturers' Association of the United States. The

[5] Circular No. 104.

Committee's draft was submitted to representatives of the paint and varnish industries and careful consideration given to their suggestions.

The specification gives the general requirements as to performance, leaving the question of specific composition an open one so as to permit a wide range of sources for the material. The provisions also include statements as to the methods of sampling, laboratory examination, and preparation of reagents.

This varnish shall be composed of a high grade of asphalt fluxed and blended with properly treated drying oil and thinned to the proper consistency with a volatile solvent. It must be resistant to air, light, lubricating oil, water, and mineral acids of the concentration hereinafter specified, and must meet the following requirements:

Appearance.—Smooth and homogeneous; no livering or stringiness.

Color.—Jet black.

Flash Point (closed-cup).—Not below 30° C. (86° F.).

Action with Linseed Oil.—Varnish must mix freely to a homogeneous mixture with an equal volume of raw linseed oil.

Insoluble in Carbon Bisulphide.—Not more than 1 per cent.

Non-volatile Matter.—Not less than 40 per cent. by weight.

Fatty Matter.—Not less than 20 per cent. of the non-volatile. Must be liquid and not show any rosin by the Liebermann-Storch test.

Set to Touch.—Within 5 hours.

Dry hard and Tough.—Within 24 hours.

Toughness.—Film on metal must withstand rapid bending over a rod 3 mm. (⅛ inch) in diameter.

Working Properties.—Varnish must have good brushing, flowing, covering, and levelling properties.

Resistance to Water.—Dried film must withstand cold water for 18 hours.

Resistance to Oil.—Dried film must withstand lubricating oil for 6 hours.

Resistance to Mineral Acids.—Dried film must withstand action of the following acids for 6 hours: Sulphuric acid, specific gravity 1.3 (about 40 per cent.). Nitric acid, specific gravity 1.22 (about 35 per cent.). Hydrochloric acid, specific gravity 1.09 (about 18 per cent.).

RECOMMENDED SPECIFICATION FOR COMPOSITE THINNER FOR THINNING SEMIPASTE PAINTS WHEN THE USE OF STRAIGHT LINSEED OIL IS NOT JUSTIFIED.[6]

[ABSTRACT.]

THIS specification was prepared under the auspices of the Bureau of Standards by the U. S. Interdepartmental Committee on Paint Specification Standardization, September 27, 1920. The Committee consisted of representatives of the War, Navy, Agriculture, Interior, Post Office, Treasury, and Commerce Departments, the Panama Canal, and the Educational Bureau of the Paint Manufacturers' Association of the United States. The Committee's draft was submitted to representatives of the paint and varnish industries and careful consideration given to their suggestions.

The specification gives the general requirements as to performance, leaving the question of specific composition an open one so as to permit a wide range of sources for the material. The provisions also include statements as to the methods of sampling, laboratory examination, and preparation of reagents.

This specification covers a composite thinner which contains in one liquid drying oil, drier, and volatile thinner. The composite thinner must meet the following requirements:

Appearance.—Shall be clear and free from suspended matter and sediment.

Color.—No darker than a solution of 6 g. of potassium dichromate in 100 c.c. pure sulphuric acid of specific gravity 1.84.

Odor.—Not offensive, either in bulk or in its subsequent use in paint mixtures.

Mixing with Linseed Oil.—When mixed in any proportion with pure raw linseed oil meeting the specifications of B. S. Circular 82, the resulting mixture shall be clear and shall show no separation or precipitation on standing 18 hours.

Drying.—When flowed on glass, the composite thinner shall set to touch in not more than 4 hours and dry hard in not more than 6 hours. When mixed with an equal volume of pure raw linseed oil, the resulting mixture when flowed on glass shall set to touch in not more than 6 hours and dry hard in not more than 8 hours.

[6] Circular No. 102.

Toughness.—The film on glass after baking for 6 hours at 105 to 110° C. (221 to 230° F.) shall be glossy, tough, and elastic.

Non-volatile Matter.—Not less than 50 per cent. by weight.

Acid Number.—Not more than 12, calculated to basis of non-volatile matter.

RECOMMENDED SPECIFICATION FOR SPAR VARNISH.[1]

[ABSTRACT.]

THIS specification was prepared under the auspices of the Bureau of Standards by the U. S. Interdepartmental Committee on Paint Specification Standardization, September 27, 1920. The Committee consisted of representatives of the War, Navy, Agriculture, Interior, Post Office, Treasury, and Commerce Departments, the Panama Canal, and the Educational Bureau of the Paint Manufacturers' Association of the United States. The Committee's draft was submitted to representatives of the paint and varnish industries and careful consideration given to their suggestions.

The specification gives the general requirements as to performance, leaving the question of specific composition an open one so as to permit a wide range of sources for the material. The provisions also include statements as to the methods of sampling, laboratory examination, and preparation of reagents.

The varnish shall be the best long oil varnish. It must be resistant to air, light, and water. The manufacturer is given wide latitude in the selection of raw materials and processes of manufacture, so that he may produce a varnish of the highest quality. It must meet the following requirements:

Appearance.—Clear and transparent.

Color.—Not darker than a solution of 6 g. of potassium dichromate in 100 c.c. of pure sulphuric acid, specific gravity 1.84.

Flash Point (closed-cup).—Not below 30° C. (85° F.).

Non-volatile Matter.—Not less than 40 per cent. by weight.

Set to Touch.—In not more than 5 hours.

Dry Hard and Tough.—In not more than 24 hours.

Toughness.—Film on metal must stand rapid bending over a rod 3 mm. (⅛ inch) in diameter.

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[1] Circular No. 103.

Working Properties.—Varnish must have good brushing, flowing, covering, and levelling properties.

Water Resistance.—Dried film must withstand cold water for 18 hours and boiling water for 20 minutes without whitening or dulling.

Durability.—The purchaser reserves the right to require that the durability of deliveries must be equal to a brand or sample mutually agreed upon by buyer and seller.

NOTE.—When durability tests are required, such tests will be made on each sample; but in cases where the testing laboratory has previous data on the same brand of varnish, acceptance or rejection of a given sample may be provisionally based on the last completed test of the brand of varnish in question.

RECOMMENDED SPECIFICATION FOR LIQUID PAINT DRIER.[8]

[ABSTRACT.]

THIS specification was prepared under the auspices of the Bureau of Standards by the U. S. Interdepartmental Committee on Paint Specification Standardization September 27, 1920. The Committee consisted of representatives of the War, Navy, Agriculture, Interior, Post Office, Treasury, and Commerce Departments, the Panama Canal, and the Educational Bureau of the Paint Manufacturers' Association of the United States. The Committee's draft was submitted to representatives of the paint and varnish industries and careful consideration given to their suggestions.

The requirements include methods of sampling, laboratory examination, and also basis of purchase.

This specification applies both to straight oil drier—that is, material free from resins or "gums"—and to Japan drier; that is, material containing varnish "gums."

The drier shall be composed of lead, manganese, or cobalt, or a mixture of any of these elements combined with a suitable fatty oil, with or without resins or "gums," and mineral spirits or turpentine, or a mixture of these solvents. It shall be free from sediment and suspended matter. The drier when flowed on metal and baked for 2 hours at 100° C. (212° F.) shall leave an elastic

[8] Circular No. 105.

Toughness.—The film on glass after baking for 6 hours at 105 to 110° C. (221 to 230° F.) shall be glossy, tough, and elastic.

Non-volatile Matter.—Not less than 50 per cent. by weight.

Acid Number.—Not more than 12, calculated to basis of non-volatile matter.

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The specification gives the general requirements as to performance, leaving the question of specific composition an open one so as to permit a wide range of sources for the material. The provisions also include statements as to the methods of sampling, laboratory examination, and preparation of reagents.

The varnish shall be the best long oil varnish. It must be resistant to air, light, and water. The manufacturer is given wide latitude in the selection of raw materials and processes of manufacture, so that he may produce a varnish of the highest quality. It must meet the following requirements:

Appearance.—Clear and transparent.

Color.—Not darker than a solution of 6 g. of potassium dichromate in 100 c.c. of pure sulphuric acid, specific gravity 1.84.

Flash Point (closed-cup).—Not below 30° C. (85° F.).

Non-volatile Matter.—Not less than 40 per cent. by weight.

Set to Touch.—In not more than 5 hours.

Dry Hard and Tough.—In not more than 24 hours.

Toughness.—Film on metal must stand rapid bending over a rod 3 mm. (⅛ inch) in diameter.

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[1] Circular No. 103.

Working Properties.—Varnish must have good brushing, flowing, covering, and levelling properties.

Water Resistance.—Dried film must withstand cold water for 18 hours and boiling water for 20 minutes without whitening or dulling.

Durability.—The purchaser reserves the right to require that the durability of deliveries must be equal to a brand or sample mutually agreed upon by buyer and seller.

NOTE.—When durability tests are required, such tests will be made on each sample; but in cases where the testing laboratory has previous data on the same brand of varnish, acceptance or rejection of a given sample may be provisionally based on the last completed test of the brand of varnish in question.

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The requirements include methods of sampling, laboratory examination, and also basis of purchase.

This specification applies both to straight oil drier—that is, material free from resins or "gums"—and to Japan drier; that is, material containing varnish "gums."

The drier shall be composed of lead, manganese, or cobalt, or a mixture of any of these elements combined with a suitable fatty oil, with or without resins or "gums," and mineral spirits or turpentine, or a mixture of these solvents. It shall be free from sediment and suspended matter. The drier when flowed on metal and baked for 2 hours at 100° C. (212° F.) shall leave an elastic

[8] Circular No. 105.

film. The flash point shall be not lower than 30° C. (85° F.) when tested in a closed-cup tester. It shall mix with pure raw linseed oil in the proportion of 1 volume of drier to 19 volumes of oil without curdling, and the resulting mixture when flowed on glass shall dry in not more than 18 hours. When mixed with pure raw linseed oil in the proportion of 1 volume of drier to 8 volumes of oil, the resulting mixture shall be no darker than a solution of 6 g. of potassium dichromate in 100 c.c. of pure sulphuric acid of specific gravity 1.84.

LIME: DEFINITIONS AND SPECIFICATIONS.[9]

[ABSTRACT.]

LIMESTONES are classed as high-calcium or magnesian according to the ratio of lime to magnesia which they contain. According to their physical structure, they vary from marble to chalk. Crushed stone of various sizes is used for blast-furnace flux, aggregate for concrete and asphalt, ballast, road-metal, sand, whiting, etc. It is also a basic raw material used in the manufacture of cement, glass, pottery, etc.

Agricultural lime, used as a fertilizer, may be ground limestone, quicklime, or hydrated lime.

Quicklime is made by burning limestone. It is used as a building material, as an ingredient of mortar and plaster. Slaked lime is made by adding water to quicklime to form a putty.

Hydrated lime is made by adding just enough water to quicklime to form a dry powder. It is used as a building material instead of quicklime, and also as an addition to cement mortars and concretes.

Both quicklime and hydrated lime are used as basic raw material in the manufacture of paper, sugar, bleaching powder, alkalies, etc.

Air-slaked lime is worthless as a building material and is seldom an article of commerce.

Quicklime is shipped in barrels, holding 180 or 280 pounds net; hydrated lime in paper bags holding 50 pounds.

The quantities of lime required for making plaster and mortar are given, as well as the amount for use as fertilizer. A formula for making whitewash is included.

[9] Circular No. 106.

Hydrated lime should contain not more than 5 per cent. impurities, nor 3 per cent. carbon dioxide. It should be of such fineness that not more than ½ per cent. shall remain on a No. 30 sieve, nor more than 15 per cent. on a No. 200 sieve. It should pass the prescribed steaming test for soundness.

CAUSES AND PREVENTION OF THE FORMATION OF NON-CONDENSIBLE GASES IN AMMONIA ABSORPTION REFRIGERATION MACHINES.[10]

By E. C. McKelvey and Aaron Isaacs.

[ABSTRACT.]

IN the experiments conducted at the Bureau of Standards the conditions existing during the operation of an ammonia absorption refrigeration machine were duplicated. It was found that the presence of the non-condensible gases that cause so much trouble in the operation of these plants is due to either or both of these causes: namely, (1) leaks of air into the system, and (2) the corrosive action of the aqua ammonia on the metal of the plant.

If the "foul" gas is mainly nitrogen, the gas is derived from air that is leaking into the system. The oxygen originally present in the air is quickly used up when the plant is operating and so will be present in only a very small percentage of its original amount. If the foul gas is hydrogen, the cause is corrosion by the ammoniacal liquor. Pure aqua ammonia will not cause gas formation; but if salts of such weak acids as acetic or carbonic acid are present in the "aqua," the corrosive action will continue during the life of the charge. If the gas contains both nitrogen and hydrogen, both causes are present.

The corrosive action of impure aqua may be completely stopped by the addition of either sodium or potassium dichromate to the aqua in the plant. The dichromate is conveniently added in the form of a concentrated solution, and gas formation will be stopped if the salt is added to the extent of 0.2 per cent. of the weight of the aqua present. It is best to add the dichromate to the charge in all plants, as its presence decreases the very small amount of gas caused by even the highest grade ammonias.

[10] Technologic Paper No. 180.

Gum Arabic.—The preparation and properties of gum arabic are described by J. A. RIDGWAY in the *Canadian Chemical Journal*, 1920, iv, 330–335. The gum is obtained from certain species of the genus *Acacia*. The trees may be tapped when three years old, and are most productive between seven and fifteen years of age. In tapping a tree, strips of its outer bark are removed, each strip is approximately two to three feet long by one to three inches broad. The gum slowly exudes as a liquid, which gradually hardens, and at the same time loses moisture. The tapping is made during the dry season, and the gum is removed from the tree from six to eight times during the season. The same tree is not tapped two years in succession, as a rule. If the gum contains more than 20 per cent. of water, it is tough and difficult to grind; if it contains less than 12 per cent. of water, it is too friable, and crushes during transportation. The gum is soluble in cold water, but usually contains 1 to 2 per cent. of impurities which are insoluble in that solvent. The solution is optically active and usually rotates the plane of polarized light to the left. Chemically, the gum is the metallic salt of a complex organic acid. The bases form 3 per cent. of the gum, and are the oxides of calcium, magnesium, and potassium. The complex organic acid, with which these bases are combined, may be split into simpler organic compounds; one of its molecules yields one molecule of arabic acid, two molecules of arabinose, and four molecules of galactose. The value of a given sample of the gum in the arts depends largely on the viscosity of its solution in water. Most of the gum imported into Canada is known as "Natural" and contains fragments of bark. The grade usually imported into the United States is termed "cleaned" and is free from bark and straw. Other grades are "cleaned and sifted," from which dust and sand as well as bark and straw have been removed, and "bleached," which has been rendered almost pure white by prolonged exposure to the rays of the sun.

J. S. H.

Lobinol—the Poison of Poison Oak.—JAMES B. MCNAIR (*Journal of the American Chemical Society*, 1921, xliii, 159–164) has extracted a dermatitant, or poison, producing inflammation of the skin, from the poison oak *Rhus diversiloba*. The bark was extracted with alcohol; and the extracted poison was purified by successive treatments with petroleum, ether, alcohol, sodium chloride brine, and distilled water. The poison apparently is an unsaturated compound of the aromatic series, containing carbon, hydrogen, and oxygen; it reacts like a phenol, and may contain two hydroxyl groups in the ortho position. On account of its phenolic nature, it has been named lobinol.

J. S. H.

NOTES FROM THE RESEARCH LABORATORY EASTMAN KODAK COMPANY.*

A COLORIMETER OPERATING ON THE SUBTRACTIVE PRINCIPLE.[1]

By L. A. Jones.

[ABSTRACT.]

In this article a new type of colorimeter operating on the subtractive principle of color mixture is described. By means of a telescopic element an image of the object whose color is to be measured is formed in the plane of the photometric cube of the instrument. In this way one-half of the photometric field is illuminated by light of the color that is to be analyzed. The other part of the photometric field is filled with light the color of which can be varied so as to match that of the unknown. As a source of this light a small incandescent automobile headlight lamp is used, operated at constant voltage, and screened with a filter of such quality that the transmitted light matches noon sunlight in color, noon sunlight being defined as standard white. Between this lamp and the photometric cube are placed four gelatine wedges, three of which are colored, and one of neutral tint, the neutral tint wedge being used for adjusting the intensity factor in the comparison field. The three colored wedges used are the attractive primaries, namely, minus green, or magenta; minus blue, or yellow; and minus red or blue-green, these colors being complementary to the three-color additive primaries. Any unknown color can be matched by using two of the colored wedges in conjunction with the neutral tint wedge, and a complete specification of color is therefore obtained by giving the scale readings of the three wedges used. In this way a numerical specification of color in terms of the constants of the instrument can be obtained. Such a determination is not a true specification of color as such, but by means of suitable calibration tables these readings can be

* Communicated by the Director.

[1] *Jour. Opt. Soc. Amer.*, November, 1920, p. 420. Communication No. 105, from the Research Laboratory of the Eastman Kodak Company.

converted into the absolute specification of color in terms of hue, saturation, and an intensity factor.

For convenience in measuring the color of various materials, special attachments are provided with another standardized lamp for illumination of the samples. As a standard of white against which the working lamps may be checked from time to time, a standardized lamp with an adjusted filter is provided in a suitable housing which may be attached to the instrument. By means of this the proper operating current for the working lamps may be determined at any time. The monochromatic analyses of the three colored wedges used in the instrument are given in graphic form in the paper.

PHOTOGRAPHIC SHARPNESS AND RESOLVING POWER.[1]

By F. E. Ross.

THE paper begins with a summary of the more important relations between the fundamental photographic variables. It is shown how to calculate the sharpness of any image solely from the gamma of the emulsion and from the rate of growth of the image with exposure. The important practical case of variation of sharpness with the color of the light is thoroughly discussed. While actual measurements of the variation of sharpness with wave-length and with time of development prove the theoretical equation derived, to be but a first approximation; the equation indicates that to secure sharp images emulsions with both high contrast and low turbidity should be selected, also those whose characteristic curves have a small "toe." Various secondary factors which affect sharpness are discussed. Tugman's method of measurement was improved and extended to densities of about 3. A theoretical formula is derived to show the variation of the resolving power of a photographic plate with the sharpness and the grain size. As an illustration, physical development of a Seed 23 plates gives images with one-fifth the sharpness obtained by chemical development, yet the grains were so much smaller that the resolving power was 20 per cent. more. The theory also explains observed variations with time of development and with wave-length, the effect of intensification, etc. By taking pains to

[1] *Astrophys. J.*, November, 1920. p. 201. Communication No. 90, from the Research Laboratory of the Eastman Kodak Company.

secure fine grains, the resolving power of a wet collodion plate may be made almost equal to the theoretical maximum for the lens used. It is suggested that astronomers are inclined to overestimate the advantage of small grain-size; for the true resolving power of some coarse-grained emulsions is far ahead of that obtainable with large telescopes. As a rule, what is needed is rather higher speed than better resolving power.

Preliminary Results of Ocean Magnetic Observations on the Carnegie from St. Helena to Cape Town and Thence to Colombo, Ceylon, April to June, 1920. J. P. AULT, Commander. (*Terrestrial Magnetism and Atmospheric Electricity,* September, 1920.)—The *Carnegie* continues to put a good, substantial, magnetic girdle round the earth in this voyage of 6665 nautical miles of forty-one days' length. Declination observations were made twice daily, while the determination of inclination and of horizontal intensity was made only once per day. The differences between the observed values and the corresponding quantities recorded in U. S. Hydrographic Office Charts for 1920, in British Admiralty Charts for 1907, and with the Reichs-Marine-Amt Charts for 1910 and 1905 are tabulated. The departure of the German charts from the fact is especially noticeable in the case of the inclination. At one place not far from St. Helena it amounted to more than ten degrees, while the maximum difference for the British chart was 5.1° and for the American 3.3°, these two maxima occurring at the same spot about thirteen days before Colombo was reached. In declination the largest error of the British chart seems to be 2.3°, of the German 5.6°, and of the American 3.3°.

There is a hint of trouble with the crew at Cape Town, where the local authorities "gave the *Carnegie* every consideration in the way of free dockage, free pilotage and free towboat service, a courtesy very much appreciated."

G. F. S.

Absorbent Cotton.—Purified or absorbent cotton is almost pure cellulose. Standard requirements for absorbent cotton are suggested by A. WAYNE CLARK, R. O. SMITH, and LEROY FORMAN (*Journal of the American Pharmaceutical Association,* 1920, ix, 958–965). It should be free from acids, alkalies, and dyes, should contain not more than 0.2 per cent. of ash, not more than 0.25 per cent. of water-soluble solids, and not more than 0.6 per cent. of fatty matter, and should become wet and sink immediately if compressed in the hand, then thrown on the surface of water which has a temperature of 25° C.

J. S. H.

The Use of Wood as Fuel in Industry. (*Le Genie Civil,* December 11, 1920.)—In March, 1920, the French minister of Public Works appointed a commission to study the utilization of fuel to the best advantage—a pressing necessity in a country whose coal mines had been so largely rendered unproductve by the German invaders. This wide field was divided among three sub-committees to which were allotted respectively the following subjects of consideration: The reduction of the use of coal by steam engines; the economizing of fuel in metallurgy and in industries on a large scale; and last, inventions and special processes (pulverization and gasefication of coal, etc,). The Ministry of Public Works is to publish from time to time the important findings of the commission. Thus from the second of the above named sub-committees comes the report on wood, prepared by M. Cornu-Thenard.

It is, to say the least, difficult to get sufficient supplies of fuel from countries outside of France and all such importation helps to make the balance of trade against that country still worse.

It is, therefore, wise to try to use the available wood found in the country and its colonies. There are in France about 10,000,000 hectares of forest (1 hectare equals 2.47 acres), and the colonies possess ten times as great an area of woodland. Before the war France produced annually 35,000,000 steres (1 stere equals 35.3 cu. ft.; 3.6 steres equal 1 cord) of firewood. Not so much can now be got from the forests, but this loss would be about made up if the wood derived from hedges and from trees along canals and roads be counted in. Owing to the high cost of fuel the wood crop is better looked after than formerly. From 3 to 5 steres of wood will give as many calories as a ton of coal, and the wood is cheaper than the equivalent coal in the locality where it is cut.

The heating power of wood is a function of its moisture content and methods of drying it are discussed. The ashes of a ton of wood give more than 7 pounds of alkaline carbonate, available for fertilizer. There are numerous drawbacks to the employment of wood, such as greater cost of handling, greater storage space needed, greater fire risk, and higher relative cost of shipment. For these reasons it is chiefly in well-wooded regions alone that wood can be expected to replace coal. It is not, therefore, surprising to read that in Alsace wood is used to fire boilers and that in Franche-Comté it has been used in the Martin steel works. The Commission recommends that managers of industrial plants consider carefully the claims of wood and, further, that in the rationing of fuel to the various parts of France the supply of available wood be considered.

G. F. S.

NOTES FROM THE U. S. BUREAU OF CHEMISTRY.*

CANTALOUPE SEED OIL.[1]

By Walter F. Baughman, Dirk Brauns, and George S. Jamieson.

[ABSTRACT.]

AN oil obtained by means of the oil expeller from a large sample of cantaloupe seed (*Cucumus melo*), from Imperial Valley, Calif., was investigated. The cold-pressed oil has a pale yellow color and a pleasant fruity taste. Although the oil had stood at room temperature for two years, it had no trace of rancid odor or taste.

The chemical and physical characteristics were found to be as follows:

Specific gravity, at 25°/25° C.	0.9210
Refractive index at 20° C.	1.4725
Iodine number (Hanus)	125.9
Saponification value	192.3
Reichert-Meissl number	0.33
Polenski number	0.26
Acetyl value	15.8
Acid value	.43
Unsaponifiable matter (per cent.)	1.1
Soluble acids (per cent.)	0.4
Insoluble acids (per cent.)	94.
Saturated acids (per cent.)	14.3
Unsaturated acids (per cent.)	80.2

The chemical composition of the oil was found to be as follows:

Glycerides of:	
Myristic acid	0.3
Palmitic acid	10.2
Stearic acid	4.5
Oleic acid	27.2
Linoleic acid	56.6
Unsaponifiable matter	1.1

* Communicated by the Chief of the Bureau.

[1] Published in *J. Am. Chem. Soc.*, 11 (1920), 2398.

SUGAR-CANE JUICE CLARIFICATION FOR SYRUP MANUFACTURE.[1]

By J. K. Dale and C. S. Hudson.

[ABSTRACT.]

AN investigation of methods now used for manufacturing cane syrup showed that it is possible to produce a superior article by clarification of the sugar-cane juice with infusorial earth. This method of clarification is feasible in any factory using steam as the source of power and results in an excellent quality of syrup. Such syrup has a milder flavor than the present Louisiana type and is lighter in color and cleaner than the Georgia type of syrup.

HYDROLYSIS OF THE GLOBULIN OF THE COCOANUT, COCOS NUCIFERA.[2]

By D. Breese Jones and Carl O. Johns.

[ABSTRACT.]

THE total globulin of the cocoanut was hydrolyzed by boiling with 20 per cent. hydrochloric acid for 36 hours and the resulting amino-acids have been determined.

By changing the order of procedure usually followed in connection with protein hydrolysis, and by applying several rather recently described methods, 78.15 per cent. of the hydrolysis products of the protein used has been identified and determined.

The order of procedure followed in the isolation and determination of the animo-acids was as follows: Removal of the hexone bases with phosphotungstic acid; separation of most of the glutaminic acid as the hydrochloride; precipitation of the remaining di-basic amino-acids as their calcium salts; extraction of proline and peptide anhydrides with absolute alcohol; esterification of the remaining amino-acids by means of the lead salt method of Foreman; fractional distillation of the esters under reduced pressure; and, finally, regeneration and isolation of the amino-acids in the usual manner.

The following percentages of amino-acids were found: Glycine, trace; alanine, 4.11; valine, 3.57; leucine, 5.96; proline, 5.54; phenylalanine, 2.05; aspartic acid, 5.12; glutaminic acid, 19.07; hydroxyglutaminic acid, 0.00; serine, 1.76; tyrosine, 3.18; cystine, 1.44; arginine, 15.92; histidine, 2.42; lysine, 5.80; tryptophane, present; leucylvaline anhydride, 0.64; ammonia, 1.57.

[1] *U. S. Dept. Agr. Bull., 921*, issued Nov. 9, 1920.

[2] Published in *J. Biol. Chem.*, **44** (1920), 291.

NOTES FROM THE U. S. BUREAU OF MINES.*

TREATING NATURAL-GAS GASOLINE TO MEET THE "DOCTOR TEST."

By D. B. Dow.

THE problem of making natural-gas gasoline that will pass the test for objectionable sulphur compounds, known as the "doctor test," has been in the past a matter of no importance to the manufacturers of casing-head or absorption gasoline, because their market was limited to refineries, which mixed the product with "straight-run" gasoline and purchased it on a gravity or distillation basis. Recently an export market has opened for this type of gasoline, so it is now desirable that it pass the "doctor test."

The Bureau of Mines has worked out, at its petroleum station at Bartlesville, Okla., a cheap and efficient method for treating the gasoline to render it "sweet" to the doctor test. The method is, briefly, scrubbing the gasoline with a solution consisting of 20 per cent. caustic soda, 7 per cent. litharge, with 2 or 3 per cent. powdered sulphur added, then rewashing with water. The method of application will vary in different plants, as a wide variety of scrubbing installations could be used. One simple arrangement is to introduce the gasoline at the bottom of a steel tower packed with steel shavings, and filled three-quarters full of the solution, the gasoline being drawn off at the top into a second tower containing water and steel shavings.

A fuller account is given in a recent report issued by the bureau.

CONSUMPTION OF REAGENTS USED IN FLOTATION.

By Thomas Varley.

IN April, 1919, the Bureau of Mines requested mill operators to supply information on the tonnages treated both by gravity concentration and flotation, the amount of concentrates produced by each system of milling, and the consumption of oils, acids, and

* Communicated by the Director.

other reagents used, for the year 1919. Some delay was experienced in collecting the data, but eventually returns were obtained from practically all the important plants.

The results have been recently published in tabular form by the bureau. The amount of ores of all kinds treated by flotation was 26,545,564 tons, from which 3,105,343 tons of concentrates were obtained, showing a concentration ratio of 8.55 tons into one. The total of all reagents used was 113,510,234 pounds, equivalent to 4.2384 pounds per ton of ore treated. The bulk of the ores treated was copper ore, the rest being lead and lead-silver ores, zinc ore, gold-silver ore, graphite ore, and miscellaneous ores, such as molybdenum and antimony, and complex mixed ores of various kinds.

The most generally used flotative agents for copper ores are sulphuric acid, kerosene acid sludge, and coal tars. For lead and silver ores, hardwood creosote is used most, followed by coal tar, crude petroleum, and pine oils. For zinc ores, pine oil is the most important, with copper sulphate second, and creosote third.

Miscellaneous agents used are sulphur, specially prepared fractions of coal creosote, wood creosote, and pine oil, also various sodium salts, ammonia, ammonium salts, etc.

TESTS OF MINERS' FLAME SAFETY LAMPS IN GASEOUS, COAL-DUST LADEN ATMOSPHERES.

By L. C. Ilsley.

SEVERAL writers have called attention to the possible failure of flame safety lamps in coal-dust laden air, and question the safety of a lamp tested in gas alone. Some attention has been given this question, but the practice has generally been to test lamps in gas and air mixtures only.

Before revising its official schedule for the testing of flame safety lamps, the Bureau of Mines recently conducted a series of tests with coal dust present, which indicated that under certain conditions, coal dust might have some slight effect. Partly as a result of these experiments, and partly because it would more nearly represent actual conditions in a coal mine, the bureau has decided that in its revised schedule for approval of flame lamps, a certain proportion of the tests in explosive mixtures of gas and air will be made with coal dust present. Details of the experiments are given in a recent report issued by the bureau.

MINOR NOTES.

Volatilization Tests on a Low-grade Ore.—The Intermountain experiment station of the Bureau of Mines, at Salt Lake City, which is making an extensive study of the metallurgy of the volatilization process, recently completed a series of experiments on a low-grade oxidized ore from Nevada, assaying 0.286 ounce gold, 3.4 ounces silver, and 4.5 per cent. lead. The experiments showed that 80 per cent. of the gold, 75 per cent. of the silver, and 76 per cent. of the lead could be volatilized with the addition of sodium chloride alone. The use of a small amount of calcium chloride in addition to the sodium chloride, increased these recoveries by about 10 per cent.

Uranium Ore Deposit.—It is reported that a mining company has opened and is developing a uranium property near Lusk, Wyoming. The ore is an unusual oxide of uranium, and determinations made by the U. S. Bureau of Mines experiment station at Golden, Colo., indicate that the deposit is likely to prove of importance.

Devitrification of Glass.—The devitrification, which occurs when glass is heated for working in the flame, is a surface phenomenon and is due to the separation of silica. ALBERT F. O. GERMANN, of Western Reserve University, who has studied this phenomenon, has found that devitrification is prevented if the glass be washed in dilute hydrofluoric acid prior to working in the flame. This washing removes the "weathered" surface of the glass, and thereby prevents the separation of silica. (*Journal of the American Chemical Society*, 1921, xliii, 11–14.)

J. S. H.

New Type of Organic Compound of Arsenic.—GEORGE JOSEPH BURROWS and EUSTACE EBENEZER TURNER, of the University of Sydney (*Journal of the Chemical Society*, 1920, xcvii, 1373–1383), have discovered a new group of organic compounds of arsenic. Many organic arsines in which the three hydrogen atoms of arsine, AsH_3, have been replaced by similar or dissimilar alkyl or aryl groups, readily combine with methyl-diiodo-arsine and with the corresponding ethyl and phenyl compounds to form new compounds which vary in color from pale yellow to deep orange. Each of these new additive compounds contains two atoms of arsenic in its molecule. Thus phenyl-ethyl-methyl-arsine reacts with methyl-diiodo-arsine to form the addition compound $C_6H_5.C_2H_5.CH_3As.CH_3AsI_2$. The structural formulæ of the new compounds are uncertain.

J. S. H.

Construction of a Plant for the Utilization of the Tidal Energy. (*La Nature*, October 30, 1920.)—To help to replace the loss of energy inflicted upon France by the destruction of her coal mines by the Germans there will be built at La Landriais, five miles from St. Malo in the northwest of France, a plant in which turbines will be driven by tidal water. Here on both sides of the Rance River there are natural basins which are covered by each tide. These have an area of 20,000 hectares and the tides are very high. Four dams will be built. The cycle of operations will, of course, repeat itself every twelve hours and twenty-four minutes, the tidal interval.

Two reservoirs are required, one at high level to be filled at high tide, and the other at low level to receive water from the first and to empty it into the sea at low tide. The cycle is that of Decoeur, presented to the Academy of Sciences in 1891. Let us suppose that it is low water at 1:30. The gates of the low reservoir are closed and it is shut off from the sea, but the level of the water in it rises continuously on account of the arrival of water from the higher reservoir, which passes through the turbines on its way down. At 1:30 the upper reservoir is likewise isolated from the sea. Its level falls as its water runs into the lower basin, while the level of the sea rises with the rising tide. These two levels become the same at 4 o'clock. Then the gates are opened and the high reservoir is filled up as the tide comes in. Meanwhile the turbines are kept in operation by water running through them to the basin below. At 7 o'clock, the end of dead water, the gates of the upper reservoir are closed. The water within continues to flow into the lower reservoir. At 11 o'clock the level of the water in the sea will have sunk to that of the lower basin, which has been rising ever since 1:30. The gates of the latter are opened and its water flows into the sea as its level falls. At 2 o'clock the gates of the lower basin will be again closed as they were at 1:30, twelve and a half hours before, and the same series of operations will be repeated. At neap tide 5000 horsepower will be developed, and at spring tide ten times as much. An annual output of more than 150,000,000 kilowatt hours is expected.

The practical operation of this plant will be scanned with great care, all the more because it is just here in the northwest of France that there is no stream power to be developed.

G. F. S.

America's Share of the World's Gold. (*Eng. and Mining Jl.*, December 11, 1920, p. 1129.)—Of a total accumulation through the ages of $8,000,000,000 in monetary gold, the United States is estimated to hold $2,500,000,000, or 30 per cent., of the world's supply. Gold holdings were increased greatly during the war because of the heavy shipments of gold made by other nations to the United States in payment for commodities.

THE FRANKLIN INSTITUTE.

(Proceedings of the Annual Meeting held Wednesday, January 19, 1921.)

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, January 19, 1921.

PRESIDENT DR. WALTON CLARK *in the Chair.*

Additions to membership since last report, 13.

A report of Progress was presented by the Committee on Library.

The tellers of the election, Messrs. Jennings, Colvin, and Picolet, submitted the report of the ballots cast for President, Vice-President, Treasurer and members of the Board of Managers, and the followng gentlemen were declared duly elected to the respective offices:

Walton Clark, President (to serve one year).

Charles Day, Vice-President (to serve three years).

Benjamin Franklin, Treasurer (to serve one year).

Charles E. Bonine, Alfred W. Gibbs, Howard S. Graham, George R. Henderson, George A. Hoadley, Lawrence T. Paul, James S. Rogers and C. C. Tutwiler, Managers (to serve three years).

The President extended the thanks of the meeting to the tellers for their services.

The President presented a statement of the work of the Institute for the fiscal year ending September 30, 1920, with the reports of the various standing committees of the Institute and the Board of Managers.

Mr. John W. Lieb, M.E., Vice-President, the New York Edison Company, was then introduced and read the paper of the evening entitled, "Leonardo da Vinci—Philosopher and Engineer." A review was presented of the activities of Leonardo da Vinci as a philosopher and engineer, with an account of his work in military, civil, mechanical and hydraulic engineering, aviation, geology, anatomy, optics and many other branches of science, literature and the arts. The lecturer pointed out that Leonardo was one of the greatest intellects of all time, assigning to him an even higher place in philosophy, science and mechanics than he already holds in the history of the graphic arts. The subject was illustrated by lantern photographs from his note-book.

A rising vote of thanks was extended to the speaker, and the meeting adjourned.

R. B. OWENS,
Secretary.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of the Stated Meeting held Wednesday, January 5, 1921.)

HALL OF THE INSTITUTE,
PHILADELPHIA, January 5, 1921.

MR. CHARLES PENROSE *in the Chair.*

The following reports were presented for final action:

No. 2744: Republic Flow Meter. The Edward Longstreth Medal of Merit to Mr. Jacob M. Spitzglass, of Chicago, Illinois.

No. 2764: Use of the A. C. Electro-Magnet in Surgery. The Edward Longstreth Medal of Merit to Professor J. Bergonie, of Bordeaux, France.

No. 2765 and No. 2766: The Franklin Medal. The Franklin Medal to Professor Charles Fabry, of the University of Marseilles, France, and Mr. Frank J. Sprague, of New York, N. Y.

The following report was presented for first reading:

No. 2761: Greaves-Etchells Electric Arc Furnace.

R. B. OWENS,
Secretary.

SECTIONS.

Section of Physics and Chemistry.—A meeting of the Section was held in the Hall of the Institute on Thursday evening, January 6, 1921, at 8 o'clock. Dr. Harry F. Keller in the Chair. The minutes of the previous meeting were approved as read.

L. I. Shaw, Ph.D., Assistant Chief Chemist of the U. S. Bureau of Mines, and formerly Captain, Chemical Warfare Service, in charge of Smoke and Incendiary Section, C.W.S., A.E.F., delivered a lecture on "Smoke and Incendiary Materiél." An account was given of the development, uses, mode of employment, and relative merits of the portable and non-portable flame projectors, smoke producers, smoke bombs, incendiary bombs and other smoke and incendiary materials used by the various belligerent nations. The lecture was illustrated with lantern slides and specimens.

After a lengthy discussion of his communication, a vote of thanks was tendered Dr. Shaw, and the meeting adjourned.

JOSEPH S. HEPBURN,
Secretary.

Mechanical and Engineering Section.—A meeting of the Section was held on Thursday evening, January 13, 1921, in the Hall of the Institute. Mr. Coleman Sellers, Jr., in the Chair.

The paper of the evening on "The Modern Cargo Vessel" was presented by Mr. William Gatewood, of the Newport News Shipbuilding and Dry Dock Company, Newport News, Virginia. An outline was given of the history and development of cargo vessels and their importance in world economics. The present types were discussed as well as the effect of their material, size, speed,

construction and equipment on their usefulness. Some of the problems involved in their building and operation were discussed and the importance of proper governmental action if the home port of the vessel carrying our cargo is to be in this country instead of abroad, as it was before the war. The subject was illustrated by lantern slides.

After a brief discussion the thanks of the meeting were extended to the speaker.

Adjourned.

R. B. OWENS,
Secretary.

MEMBERSHIP NOTES.

ELECTIONS TO MEMBERSHIP.

(Stated Meeting, Board of Managers, January 12, 1921.)

RESIDENT.

MISS CAROLINE D. BLACKBURN, 207 South Third Street, Philadelphia, Pennsylvania.

MR. WALTER J. COPPOCK, Box 2, Logan Hall, University of Pennsylvania, Philadelphia, Pennsylvania.

MR. J. W. VAN DYKE, The Wellington, Philadelphia, Pennsylvania.

MR. FRANK H. ROGERS, William Cramp & Sons Ship & Engine Building Company, Philadelphia, Pennsylvania.

NON-RESIDENT.

DR. JOSEPH S. AMES, The Johns Hopkins University, Baltimore, Maryland.

DR. ARTHUR L. DAY, Carnegie Institution, Washington, D. C.

DR. HENRY PHELPS GAGE, Corning Glass Works, Corning, New York.

DR. M. LUCKIESH, Nela Park, Cleveland, Ohio.

DR. P. G. NUTTING, Westinghouse Electric & Manufacturing Company, East Pittsburgh, Pennsylvania.

DR. M. POSER, 16 Vick Park B, Rochester, New York.

DR. CHARLES SHEARD, Southbridge, Massachusetts.

PROF. JAMES P. C. SOUTHALL, Columbia University, New York City, New York.

ASSOCIATE.

MR. DANIEL BACHE, 2102 Pine Street, Philadelphia, Pennsylvania.

CHANGES OF ADDRESS.

MR. CHARLES G. ADSIT, 555 Electric & Gas Building, Atlanta, Georgia.

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MR. J. B. PORTER, 1527 Spruce Street, Philadelphia, Pennsylvania.

MR. J. R. WATKINS, Apartment 6 Belmont, College Hill, Cincinnati, Ohio.

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BOOK NOTICES.

DAS KUGELPHOTOMETER. (ULBRICHT'SCHE KUGEL.) von Dr. Ing E. h. Dr. Richard Ulbricht. 110 pages, 31 illustrations, 3 tables and contents. Berlin, R. Oldenbourg, 1920. Price, 24 marks in paper, 28 marks bound.

The literature on the subject of the Ulbricht sphere, as used in photometry, is so scattered that a comprehensive discussion by the original inventor should be very welcome, particularly at this time when the sphere has found such extensive application in commercial as well as standard practice. While various forms of integrating photometers have been invented and described, prior to the last few years, their use in practice was almost entirely confined to the measurement of arc lamps or lamps and reflectors. But the impracticability of rotating the gas-filled tungsten incandescent lamps brought them into the same class as the arc lamps, and so greatly increased the demand for an instrument measuring total flux. The simplicity of the so-called "sphere" photometer has led to its adoption by lamp factories as well as standardizing laboratories.

The book is divided into ten chapters, the first of which is devoted to a brief historical survey. Credit is given to Dr. W. E. Sumpner, who described the principle of the sphere as early as 1892–3, but without referring to its use in photometric practice. The author was led to an independent discovery through a study of the laws of light distribution in interiors. The second chapter discusses the fundamental theory on which is based the application of the sphere to the measurement of total flux and mean spherical candlepower. The next chapter describes the early investigations in which the effect of extreme differences in the light distribution of the source, the position of the source in the sphere, and the effect of a translucent instead of an opaque shielding screen are tested.

The theory of the sphere assumes a source of light without any obstructing parts which would absorb or otherwise influence the free reflection of light from and to all points on the inner surface of the sphere. As it is obviously impossible to attain this condition in an actual instrument, it becomes necessary to determine the effect of the presence of "foreign" bodies, such as the shielding screen, the lamp holder and, when used, other screens and a second lamp. A chapter is devoted to this broad subject and another chapter to the shielding screen, whose size, position and character, translucent or opaque, are very important factors in the relation of the illumination of the sphere window to the total flux. The window itself is discussed in a separate chapter.

The general theory also assumes an interior surface which is perfectly diffusing, *i.e.*, obeys Lambert's cosine law, and as such a surface is not obtainable in practice, the effect of departure from the law, due to the paint used to coat the surface, must be ascertained. In this connection the author refers freely to the work of E. Dyhr, who in 1910 made a somewhat extended investigation both of the effect of departure from Lambert's law, and of lack of whiteness in the paint. For those who wish to make a sphere or wish to repaint one, a recipe is given for a paint adopted by the Lichtkommission des Verbandes Deutscher Elektrotechniker.

The remaining chapters are devoted to special uses of the sphere, such as the measurement of mean hemispherical candlepower, to methods of measurement, and finally to the construction of the sphere, the materials used, ventilation, size, arrangement of equipment, and special devices, such as the compensating screen of Benford.

While not much has been published in this country on the subject of the integrating sphere, it seems somewhat regrettable that in a book devoted to the subject no reference is made to the analytical and experimental work of Chaney and Clark and to that of Rosa and Taylor at the Bureau of Standards, both presented before the U. S. Illuminating Engineering Society. The book could be made more complete in subsequent editions by the inclusion of a description of work done in England on the so-called "Box Integrator," which is a modification of the idea of the sphere. It may be added for the benefit and encouragement of the reader who is not an adept in the German language that the diction is not difficult.

F. E. CADY.

THE HUMAN MOTOR OF THE SCIENTIFIC FOUNDATIONS OF LABOR AND INDUSTRY. By Jules Amar, D.Sc., Director of the Industrial Laboratory at the Conservatoire National des Arts et Métiers. Paris, 8vo., 466 pages, contents, index, 309 illustrations and numerous tables. New York, E. P. Dutton & Co. $10.00 net.

It is somewhat difficult to appraise this volume. Originally appearing in France, in 1914, the English translation had to be deferred on account of the war. The names of the translators, Elsie P. Butterworth and George F. Wright, appear only in small type on the verso of the title-page, without information as to their relation to the subject in hand. The purpose of the book is, as the author says in the preface, to bring together in one volume all the physical and physiological elements of industrial work. Taylor's system of efficiency

is looked upon very favorably by the author, although it seems that in the United States its popularity has not been maintained at the original level.

Eighty-four pages are taken up with a discussion of general principles—statics and kinetics, dynamics and energetics, resistance of materials and elasticity. About eight pages are devoted to the structure and functions of the "Human Machine." Then follow sections on "Human Energy," "Man and His Environment," "Experimental Methods," and the closing section on "Industrial Labor." The extent of literature consulted is enormous, almost every page has several foot-note references, in which French, German and English authorities are mentioned. One notes with pleasure that American work is frequently quoted.

The book is essentially a treatment of the human being as a motor, and a discussion of the conditions under which the greatest efficiency can be obtained. As a general conclusion the human motor is stated to be probably an "electro-capillary" engine, in which nervous excitation modifies the superficial tension and produces contraction, but the nature of the nervous agent and the origin of human motive power are not yet known. The efficiency of the human motor is high, and the average duration of its activity is greater than that of any inanimate prime mover, the human motor being capable of self-repair. Brief stoppage of nutrition does not immediately suspend the action of the human machine, as does the stoppage of supplies to inanimate motors. Further, the human machine is capable of improvement, while the efficiency of an inanimate machine is best when new. As a criticism of Taylor's system, the author says that Taylor does not give sufficient weight to the physiologic factor. Naturally Doctor Amar is most interested in the improvement of efficiency of the French workman and soldier. An allusion to the defeat at Sedan is evidence that the present English text is derived from a work written before the late war.

The work contains a large amount of information, much of it in small details. It seems to have been well translated. Typographic errors are few, and not misleading, so far as the reviewer has noted.

HENRY LEFFMANN.

PRIESTLEY IN AMERICA. 1794–1804. By Edgar F. Smith, University of Pennsylvania. 12mo. 173 pages. Philadelphia, P. Blakiston's Son & Co. $2.00 net.

Doctor Smith has turned his attention for several years of late to the history of chemistry in America, and has brought into notice many highly interesting facts. Among these is that the first society, so far as records go, for the special study of chemistry was formed in Philadelphia. Every citizen of the United States knows that Philadelphia was for many years the leading city, both in population and importance, in this part of the world. It lost its place as the capital of the nation by reason of a "deal" between certain southern congressmen and their northern colleagues. The story can be found in the records.

The story of Priestley in America has many points of interest. He was not only an eminent chemist, but he took active part in certain religious movements of the time. In those days the minds of men and women seem to have

taken religious dogmas more seriously, as a rule, than do the people at large to-day. Piety, deep and sincere, is still much in evidence, but familiarity with the general run of educated people, and especially scientists, shows a general indifference to the points of dogma which, after all, constitute the substance of a religious faith.

Priestley began his active career as a Presbyterian minister, but theologic ideas that are commonly called Unitarian seemed to develop early in his preaching. He acquired a knowledge of the semitic languages. He began, about 1760, to write tracts opposing the attitude of the British government towards the colonies. He took up a line of research on "different kinds of air" which was part of the general development of "pneumatic chemistry," that led to so much progress in the last half of the eighteenth century. His coming to America was largely due to his favorable attitude towards the French revolution, in its early stages, and when on July 14, 1791, a dinner was arranged in Birmingham to celebrate the fall of the Bastille, he was the object of mob violence although he said that he had little to do with the affair. The mob destroyed his house and chapel and many valuable records. He retreated to London, where though safe from attack, he was not well received by many scientists. He accepted a preaching position, which he filled until 1794, when he came to the United States, arriving at New York, but finally settling at Northumberland, Pa., where he lived until his death in 1804.

Doctor Smith has searched the contemporary newspapers, documents and books and has woven the data thus obtained into a most interesting narrative of the man, whom he calls correctly a "wonderful figure in science, history, religion, politics and philosophy." In these days, when it seems to be the custom, as stated above, of educated men to be non-committal on all topics but those of their specialty or business, it is refreshing to read in Doctor Smith's book that Franklin called Priestley an "honest Heretic," and then adds: "I think, all the heretics I have known were virtuous men." Doctor Smith's view is, by the way, that Franklin developed Priestley into a man of science.

The book is one to be read straight through, by which a vivid picture can be obtained of the personality and abilities of the great chemist in exile, and also, incidentally, a picture of the curious features of the phlogiston discussion.

HENRY LEFFMANN.

PAPERS ON PAINT AND VARNISH AND THE MATERIALS USED IN THEIR MANUFACTURE. By Henry A. Gardner, Director, Scientific Section, Paint and Varnish Manufacturers' Association of the United States. 501 pages, illustrations, 8vo. Washington, D. C. Published by the author, 1920. Price, $10.

This new volume of 500 pages, profusely illustrated, comprises the work done by Mr. Gardner, at the Institute of Industrial Research, for the Educational Bureau of the Paint Manufacturers' Association of the United States and the National Varnish Manufacturers' Association during the past two years, the result of work previously done having been embodied in two earlier volumes entitled, respectively, "Paint Technology and Tests" and "Paint Researches and Their Practical Application."

As Technical Director of the Educational Bureau, engaged continuously in

research on the technology of the paint and varnish industry for the past ten or twelve years, he has had an unparalleled opportunity to familiarize himself with the subject, and has naturally become perhaps our foremost authority thereon.

The results of his researches and other work issued in the form of technical circulars and bulletins to the members of the two Associations, and later, at regular intervals, are collected and edited by Mr. Gardner and issued in permanent form. The present volume is the third of the series. It covers a wide range of subjects, all directly connected with paint or varnish technology, and many of the papers included have been adopted as regular working standards in the industry. This is especially true of the chapter entitled "Bulking Values and Yields of Pigments and Liquids Used in Paint and Enamel Manufacture," involving, as it did, over six months of work in his own laboratory and the laboratories of the Bureau of Standards. The same may be said of the "Standard Specifications of the War Department" and the "Interdepartmental Specifications" of the U. S. Government, in the preparation of which Mr. Gardner played an important part.

Of another chapter, "Illumination from Paint," it may be truly said that it has revolutionized factory practice in many industries; while the paper on the "Production of Rosin Tung Esters" introduced scientific accuracy into a procedure that, before its appearance, was largely based on guesswork and rule-of-thumb.

The TABLE OF CONTENTS is as follows:

I. Résumé of Soya Bean Oil Investigations. II. Driers for Soya Bean Oil. III. Marine Animal and Blubber Oils. IV. Miscellaneous Fish Oils. V. Changes in Oils Upon Storage. VI. New Foreign Oils. VII. Standards for Tung Oil. VIII. Hexabromide Test for Determining Purity of Linseed Oil. IX. A Method for Determining the Acid Values of Varnishes and Boiled Oils. X. The Effect of Moisture on the Drying of Oils and Varnishes. XI. Fume Loss in Boiling Oils. XII. Fume Control in the Varnish Industry. XIII. Tests of Moisture and Water-Resistance of Various Coatings on Small Boat Construction. XIV. New Exposure Tests at Atlantic City. XV. Production of Rosin Tung Esters (Tunga Resin). XVI. Bulking Values and Yield of Pigments and Liquids Used in Paint and Enamel Manufacture. XVII. Oil Absorption of Pigments. XVIII. Fineness and Texture of Pigments. XIX. Metal Powders as Pigments. XX. Primers for Aluminum and Galvanized Iron. XXI. Rare Elements as Paint Pigments. XXII. Waterproof Glues. XXIII. Quick-Drying Lacquer Coatings. XXIV. Notes on the Standardization of Mineral Spirits. XXV. An Emollient for Skin Protection in the Dope and Varnish Using Industries. XXVI. Illumination from Paint. XXVII. Dark Wall Colors for Operating Rooms. XXVIII. Notes on the Effect of Colored Light Upon Plant Growth and Pigmentation. XXIX. Metric Equivalents. XXX. Spreading Rates of Prepared Paint Products. XXXI. A Study of the Practicability of Spray Painting. XXXII. The Preservative Function of Paint and Varnish. XXXIII. Paints for the Home. XXXIV. Paint and Varnish in the Great War. XXXV. Standard Paint Specifications of the War Department. XXXVI. Interdepartmental Specifications.

G. B. HECKEL.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS.

Report No. 90. Comparison of Hector Fuel with Export Aviation Gasoline, by H. S. Dickinson, V. R. Gage and S. W. Sparrow, Bureau of Standards. 10 pages, diagrams, quarto. Washington, Government Printing Office, 1920. Aviation engine development for attaining higher power at altitude are following two principal lines, supercharging and increase in compression ratio. For the latter, fuels have been demanded which are capable of operating under compressions too high for gasoline. Among the fuels which will operate at compression ratios up to at least 8.0 without preignition or "pinking" is Hector fuel, whence a careful determination of its performance is of importance.

The Hector fuel supplied by the Bureau of Mines for use in these tests was a mixture of 30 per cent. benzol (C_6H_6) and 70 per cent. cyclohexane (C_6H_{12}), having a low freezing point, and distilling from first drop to 90 per cent. at nearly a constant temperature, about 20° C., below the average distillation temperature ("mean volatility") of the X gasoline.

This comparison of the performance of the two fuels in an aviation engine was made in the altitude chamber at the Bureau of Standards, duplicating altitude conditions up to about 25,000 feet, except that the temperature of the air entering the carburetor was maintained nearly constant at about 10° C. A Liberty 12-cylinder aviation engine was used, supplied with special pistons giving a compression ratio of 7.2 (the compression pressure measured by check-valve gauge was 170 pounds per square inch). Stromberg carburetors were used and were adjusted for each change of fuel, speed, load, and altitude, so as to give the maximum possible power with the least fuel for this power. The tests covered a speed range of 1400 to 1800 r.p.m.

The results of these experiments show that the power developed by Hector fuel is the same as that developed by export aviation gasoline at about 1800 r.p.m. at all altitudes.

Report No. 96. Statical Longitudinal Stability of Airplanes, by Edward P. Warner, Langley Memorial Aeronautical Laboratory, 28 pages, illustrations, quarto. Washington, Government Printing Office, 1920. This report, which is a continuation of the "Preliminary Report on Free Flight Testing" (No. 70), presents a detailed theoretical analysis of statical stability with free and locked controls and also the results of many free flight tests on several types of machines.

In developing the theory of stability with locked controls an expression for pitching moment is derived in simple terms by considering the total moment as the sum of the moments due to wings and tail surface. This expression, when differentiated with respect to angle of incidence, enables an analysis to be made of the factors contributing to the pitching moment. The effects of slip stream and down wash are also considered, and it is concluded that the C. G. location has but slight effect on stability, and stability is much improved by increasing the efficiency of the tail surfaces, which may be done by using an "inverted" tail plane.

The results of free flight tests with locked controls are discussed at length, and it is shown that the agreement between the experimental results and theory is very satisfactory.

The theory of stability with free controls is not amenable to the simple mathematical treatment used in the case of locked controls, but a clear statement of the conditions enables several conclusions to be drawn, one of which is that the fixed tail surfaces should be much larger than the movable surfaces.

The discussion of flight tests with free controls covers the effect of C. G. position, tail setting, and slip stream on the JN-4H and gives an analysis of the curves of forces on control stick for the VE-7, U.S.A.C.-11, and Martin transport.

PUBLICATIONS RECEIVED.

Ontario Department of Mines: Twenty-ninth annual report, being vol. xxix, 1920. Part i. Statistical Review, Mining Accidents in 1919, Mines of Ontario; Second Report of the Joint Peat Committee, A Geological Reconnaissance Into Patricia, Windy Lake and Other Nickel Areas, Halley Burian Intrusive Rocks. Part iv. Kirkland Lake Gold Area, by A. G. Burrows and P. E. Hopkins. Part vi. The Stratigraphy and Paleontology of Toronto and Vicinity. Part i by Beatrice Helen Stewart. 3 vols., illustrations, plates, maps, 8vo. Toronto, King's Printer, 1920.

U. S. Bureau of Mines: Tenth Annual Report of the Director to the Secretary of the Interior for the Fiscal Year Ended June 30, 1920. 149 pages, illustrations, plates, 8vo, Bulletin 117. Structure in Paleozoic Bituminous Coals, by Reinhardt Thiessen. 296 pages, plates, 8vo. Miners' Safety and Health Almanac, 1921, published in coöperation with U. S. Public Health Service for the use of miners. Compiled by R. C. Williams, Assistant Surgeon, U. S. Public Health Service. 48 pages, illustrations, 8vo. Monthly Statement of Coal-mine Fatalities in the United States, October, 1920, by W. W. Adams. 8 pages, 8vo. Technical paper 271. State Mining Laws on the Use of Electricity in and About Coal Mines, by L. C. Ilsley. 51 pages, 8vo. Washington, Government Printing Office, 1920.

National Advisory Committee for Aeronautics: Technical Notes: No. 26, A Variable Speed Fan Dynamometer, by Karl D. Wood, Bureau of Standards. 9 pages, plate, quarto. No. 29, Progress Made in the Construction of Giant Airplanes in Germany During the War, by A. Baumann. 11 pages, quarto. No. 30, Design of Recording Wind Tunnel Balances, by F. H. Norton, Physicist, Aerodynamical Laboratory, N. A. C. A. 6 pages, plates, quarto. No. 37, The Determination of the Effective Resistance of a Spindle Supporting a Model Aerofoil, by W. E. Davidson and D. L. Bacon, Aerodynamical Laboratory. 4 pages, plates, quarto. No. 39, High Thermal Efficiency in Airplane Service, by S. W. Sparrow, Automotive Power Plants Section, Bureau of Standards. 5 pages, plates, quarto. Washington: Committee, 1920.

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